AVIATION GASOLINE MANUFACTURE

THE PENNSYLVANIA STATE COLLEGE

Mineral Industries Series

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Van Winkle · MANUFACTURE OF AVIATION GASOLINE

Teichert · FERROUS METALLURGY, 3 VOLUMES

Aviation Gasoline
Manufacture

by

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FIRST EDITION

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

Since the advent of commercial-scale processes for the manufacture of isooctane, the production of aviation gasoline has rapidly grown into an industry within an industry. A great number of new methods for the production of various types of substances having high-antiknock values, which were generally believed to be impractical a short time ago, are now in operation and are producing large quantities of relatively pure hydrocarbon compounds which have the characteristics suitable for aviation fuel blending stocks. In addition, new processes are being developed and put into operation at an accelerated rate.

This advancement in the technique of high-antiknock motor-fuel manufacture has been spurred by the demands brought about by war conditions. Although the war program has aided in this development, the aviation-fuel industry cannot be considered a war industry because extended research before the war had already established its basis. The war merely moved ahead 10 to 20 years the logical development of aviation-fuel manufacture. Great advancements in aviation and automotive fields are certain to be made which will result in continued or greatly increased demands for fuels of 100 octane number or higher.

There has been a large amount of information published in the literature concerning the manufacture of aviation fuels, the manufacture of their components, the characteristics and performance of the fuels, and their specifications. In much of the literature concerning the manufacture of high-antiknock hydrocarbons the application of the processes described was applied principally to the production of higher antiknock motor fuels with little mention of aviation fuel. As far as the author is aware there has been no attempt to describe in detail the manufacture of aviation fuel as a definite field by itself.

The purpose of this book is to summarize the available information concerning the manufacture of aviation gasoline in such a form that it will serve as a reference for those who are interested

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in this field of refining, and to develop a fundamental discussion
of aviation gasoline manufacture presented in a logical sequence
that will serve as a textbook for those students and individuals
who are unfamiliar or only partly familiar with the subject.

In the best interests of this country at war, it is obvious that
detailed information on many of the processes described here
cannot be published at the present time.   There are at least five
new processes, or new modifications of older processes, which
have been announced but which cannot be described in detail.
Similarly, information concerning the latest specifications and
methods of test is in the restricted classification until the end of
the war.   The author hopes, however, that this book will serve
satisfactorily as a summary of existing publishable information on
aviation gasoline and that its value as a textbook on the subject
will be but slightly impaired by the necessary omissions.

The author is deeply indebted to all who have helped in survey-
ing the literature, in reading and commenting on the organi-
zation and content of the book, and in any way helping in the
writing of it.   The author also wishes to express appreciation to
the Gulf Publishing Co., the Petroleum Publishing Co., the
Petroleum Engineering Publishing Co., the American Petroleum
Institute, the Institute of Aeronautical Science, the National
Petroleum Publishing Co., and *Industrial and Engineering
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<div align="right">Matthew Van Winkle.</div>

Ann Arbor, Mich.,
   December, 1943.

APPENDIX

AVIATION GASOLINE MANUFACTURE

CHAPTER I

HISTORY AND DEVELOPMENT OF AVIATION FUEL

Aviation fuel, as it is designated today, is of fairly recent origin. In the early days of aviation, from 1903 to 1917–1918, almost anything was used in an airplane engine that would enable it to operate. During this period the quality of aviation gasoline was generally the same as that of the regular motor gasoline for automobiles and in many cases inferior to it. No generally accepted specifications were established for aviation gasoline as such.

The somewhat expanded use of airplanes in the First World War caused a definite interest in aviation fuel. After the loss of a number of them, believed to have been caused by motor failure due to improper fuel,[1] the government services in 1918 set up specifications for a suitable aviation gasoline that definitely differentiated it from motor fuel. Since that time the development of a distinctive fuel for airplane motors has kept pace with changes and improvements in the motors themselves.

The next important phase in the evolution of aviation fuel was the recognition of antiknock value and the development of suitable rating methods to determine it. This took place in the thirties, and during that period fuels of 87, 92, and finally 100 octane number were introduced and adopted for general use.

At the time of the entrance of the United States into the Second World War, the major aviation gasoline was the 100 octane grade, and it exceeded in quantity the other grades produced.

[1] See Ref. 1. Superior numbers throughout this book refer to the list of references at the end of each chapter.

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The effects that the developments in aviation during this war will have on aviation fuel are difficult to predict. It is expected that antiknock values will be extended far above the present standard of 100 with resulting increases in power and operating efficiency.

Manufacturing methods have changed radically owing to the increased quality of aviation fuel. With the development of hydrocarbon conversion processes for the production of high-octane compounds, the production of aviation fuel has become an industry within an industry.

Aviation Fuel before the First World War.—Until the year 1916, aviation fuel or motor fuel, since the same type of material was used in both automobile and airplane motors, was a material of widely varying characteristics. The principal specification was that of gravity (degrees Baumé), and the gravity of the fuel was supposed to indicate its quality. By 1916 it was recognized that this test was not a satisfactory measure of motor fuel characteristics. The U.S. Bureau of Mines undertook the study of motor gasolines being produced at that time for the purpose of establishing specifications suitable to consumers and manufacturers. These were to be based on tests that actually indicated the quality of the fuels in relation to their performance in motor operation.

In a paper by Dean,[2] the requirements for motor gasoline at that time were given as follows:

1. The gasoline should contain enough volatile material to ensure easy starting, but not enough to cause excessive evaporation losses and danger in handling and storage.

2. It should not contain heavy materials that would not vaporize and burn.

3. It should not form a residue in the motor.

4. It should be free from corrosive substances.

5. It should not have, and its combustion products should not have, a disagreeable odor.

6. It should be free of noncombustible material such as water and acid.

The specifications set up for motor and aviation gasolines as a result of this study were as given in Table 1-I.

These specifications were obviously not very strict and were merely an attempt to stabilize the gasoline boiling range within

TABLE 1-I.—SPECIFICATIONS FOR MOTOR GASOLINE 1917[2]

Acidity..................... Neutral
Color...................... Water white
Volatility:
   20% evaporated, °F., min.. 158°
   50% evaporated, °F., max.. ½ (20% point + 90% point)
   90% evaporated, °F., min.. Reported
   End point, °F., max........ 99° + 90% point
Water and sediment.......... None

certain wide limits. No consideration was made for stability, vapor pressure, and hydrocarbon-type content. Although it was generally recognized that gravity was no indication of quality, it was still to be reported. The presence of unsaturates due to addition of cracked to straight-run gasolines was detected by means of the acid heat test, iodine number, or solubility in sulfuric acid. No specification was established for this purpose, because it was believed that cracked gasoline had no harmful properties.

Aviation Fuel during the First World War.—Not many months after this country's entrance into the war it was recognized that regular motor fuel was unsatisfactory for use in airplane motors. This was found to be especially true in the case of combat airplanes and, after the loss of a number of them was attributed to improper engine performance due to unsatisfactory fuels, several cooperative studies by government agencies were started in the summer of 1917. On Aug. 2, 1917, the Bureau of Mines arranged to study fuels for airplane engines in cooperation with the Aviation Section of the Signal Corps. After a general survey, it was found that no reliable data were available on the proper fuel. Various tests were conducted at Langley, McCook, and Wright fields in actual flight tests, and an altitude chamber erected by the Bureau of Standards was used to study performance at conditions encountered at high altitudes. In addition, laboratory examinations, particularly of distillation characteristics, were conducted by both bureaus.

Several interesting results were found from these investigations. In certain types of airplane, motor gasoline gave just as satisfactory performance results as Pennsylvania "high-test." In others the fliers reported hot-running motors with the use of this type of fuel. An experimental gasoline, composed of cyclohexane, 70 per cent, and benzene, 30 per cent, seemed to

be the most satisfactory for use in fighting airplanes. This fuel evidenced suitable operating characteristics in motors having a compression ratio as high as 7.5:1, and in some cases, this allowed a 10 per cent power increase and a 1,000-ft. increase in ceiling. Other fuels distilled from selected crude oils were also satisfactory. We know now that such gasolines were of the aromatic or naphthenic type and had relatively high octane numbers. To ensure a reasonable standard of quality, inspections were conducted on aviation and motor gasolines which were shipped abroad for use of the fighting forces. Little information was published on specifications used to differentiate motor from aviation gasoline, but it is to be assumed that prewar distillation specifications applied.

It is probable that gasolines from selected crude oil bases, which experience in operation and tests by the government bureaus had indicated to be satisfactory, were demanded for use in combat airplanes.

During the war, manufacture of aviation fuel consisted of the following methods:

1. Distilling a straight-run gasoline from a suitable crude oil source and adjusting the distillation range to the loosely specified limits.

2. Distilling a straight-run gasoline and adding to it "casinghead" or natural gasoline (or adding natural gasoline to kerosene distillate).

3. Blending cracked gasoline to straight-run gasoline with or without the addition of natural gasoline.

4. Blending straight-run gasoline with benzol and alcohol.

5. Through close fractionation of a naphtha cut from selected crude oils (California and Venezuela), securing a 10-deg. boiling-range fraction to be used unblended as a fuel.

6. Manufacturing cyclohexane synthetically and blending with it benzene.

The last three methods were in an experimental state at the end of the war and were not used extensively.

It is interesting to note that cyclohexane (octane number, 83r;* blending octane number, 110r), benzene (octane number, 100+r; blending octane number, 99r), alcohol (octane number around 100), natural gasoline (octane number, 65 to 80), and

*r designates C.F.R. Research method.

straight-run gasolines from naphthenic and aromatic crude oils (60 to 80 octane number) were found from experience to give satisfactory performance. Thus, although apparently unaware of detonation effects and knocking, the users of aviation fuels were beginning to recognize differences in the effects of the different hydrocarbon types on engine performance.

Aviation Fuel 1918 to 1929.—After the war, interest in the manufacture of aviation fuel from such materials as cyclohexane ceased. This probably was due to the economic factor involved in the manufacture of such compounds. Also, the demand was not sufficient to warrant extensive developments at that time. The interest turned again to motor fuel and its quality while aviation gasoline was left to shift for itself.

In 1920, Hill and Dean[1] reported on the quality of gasoline marketed in the United States and compared the results of the 1917 survey with those of the 1919 survey, both conducted by the Bureau of Mines. Several interesting facts were presented. Between 1917 and 1919 the amount of cracked gasoline utilized almost doubled. Also, the use of natural gasoline increased greatly, owing to the widening of the volatility range of motor gasoline.

During this period many states had established specifications on gasoline (motor). No two of these agreed and all were unsatisfactory from one standpoint or another. At this time the government was using distillation specifications as shown in Table 2-I.

TABLE 2-I.—MOTOR GASOLINE SPECIFICATION
("Navy specification")

Initial B.P., °F., max	140
20%, °F., max	221
45%, °F., max	275
90%, °F., max	356
End point, °F., max	428
Recovery, %, min	95.0

The survey was used to determine the quality range of gasolines sold in this country, thereby enabling the establishment of specifications that would be suitable for general use. Much variation was found in the results of all tests used in the examination of the samples. They varied with the company producing

the gasoline, the locality from which the samples were obtained, and the season of the year.

Refining companies, particularly the larger ones, had begun to include in their shipping specifications, color, odor, unsaturation (per cent soluble in H_2SO_4), doctor test, gravity, and distillation range. Under distillation range were included initial boiling point, 20 per cent point, 50 per cent point, 90 per cent point, end point, and average boiling point.

TABLE 3-I.—U.S. GOVERNMENT SPECIFICATIONS ON GASOLINE, 1922[3,4]

	Aviation gasoline		Motor line
	Fighting grade	Domestic grade	
Color, Saybolt, min....................	25	25	16
Corrosion, copper dish	None	None	
Corrosion, copper strip			None
Distillation:			
I.B.P., °F., max.....................			131
5%, °F., range*.....................	122–149	122–167	
20%, °F., max.*.....................			221
50%, °F., max.*.....................	203	221	284
90%, °F., max.*.....................	257	311	392
96%, °F., max.*.....................	302	347	
E. P. °F., max.......................	329	374	437
Recovery, %, min....................	96.0	96.0	95.0
Loss, %, max........................	2.0	2.0	
Acidity of residue....................	None	None	
Doctor test..........................	Negative	Negative	
Gum, copper dish, mg./100 cc., max......	3.0	3.0	
Unsaturated hydrocarbons, %, max.†.....	1.0	2.0	
Water and sediment, max...............	None	None	

* Per cent recovered.
† Per cent soluble in 95 per cent H_2SO_4.

Since the unsaturation test was included, it is evident that the refiners were recognizing the fact that unsaturated (or cracked) materials caused gumming in storage and in use, and that some control on the amount of such material included (from cracked gasoline) was necessary.

In 1922 government specifications on two grades of aviation gasoline and one type of motor gasoline were published. These are found in Table 3-I. These specifications were drawn up by

a government committee on specifications working with an advisory board made up of members of various engineering societies. They were adopted on Jan. 23, 1922, amended Mar. 1, 1922, and revised Oct. 31, 1922.

In this set of specifications the qualities controlled were color, corrosiveness, and mercaptan sulfur content, volatility, stability, and suspended matter. The appearance of the copper-dish residue test and the unsaturation test indicated that some importance was being given to the effect of gum formation by the fuel consumers. The volatility range of the aviation gasolines, both fighting and domestic grades, was narrower than that of the motor gasoline. The volatility of the fighting grade was greater than that of the domestic grade.

TABLE 4-I.—U.S. GOVERNMENT SPECIFICATIONS* ON GASOLINES—1927[5]

	Aviation gasoline		Motor ʲline
	Fighting grade	Domestic grade	
Color, Saybolt, min................	25	25	
Corrosion, copper dish.............	None	None	
Corrosion, copper strip.............			None
Distillation:			
I.B.P., °F., max.................			131
5%, °F., max...................	122–149	122–167	
20%, °F., max..................			221
50%, °F., max..................	203	221	284
90%, °F., max..................	257	311	392
96%, °F., max..................	329	374	437
Recovery, %, min...............	96.0	96.0	95.0
Loss, %, max...................	2.0	2.0	
Acidity of residue................	None	None	
Doctor test.......................	Negative	Negative	
Gum, copper dish, mg./100 cc., max.	3.0	3.0	
Sulfur, %, max....................	0.10	0.10	0.10
Water and sediment...............	None	None	None

* In addition to fullfilling the listed specifications, samples of the aviation fuel had to be submitted upon request for performance tests before acceptance.

The specifications issued in 1924[5] were identical with those issued in 1922 with the exception that the specification covering the percentage of unsaturation was deleted for both aviation

gasolines and the motor gasoline, and a total sulfur content limit was added. This limited the total amount of sulfur permissible in each of the three fuels to 0.10 per cent maximum.

By 1927, no additional changes had been made in these specifications. Table 4-I shows them as of 1924–1927.

The qualification requiring that representative samples of the fuels be submitted for operation tests indicates clearly that the laboratory inspections were unable to determine definitely the quality in regard to actual performance. This requirement enabled the purchaser to determine in full-scale motor tests any unsatisfactory qualities in 'a fuel that were not detected by the laboratory test methods.

Up until 1930 the general specifications on aviation fuel did not change. In 1929 they were essentially the same as they were in 1927.

Manufacture of Aviation Fuel, 1918 to 1929.—During the period from 1918 to 1922, aviation-fuel manufacture was relatively simple for the refiner. Several similar methods were followed and consisted of

1. Fractionation of a suitable boiling-range naphtha from crude oil.

2. Fractionation or stabilization of natural gasoline to correct boiling range.

3. Fractionation of cracked gasoline to correct boiling range and blending it with straight-run gasoline or natural gasoline.

4. Addition of benzol to suitably fractionated straight-run gasoline.

During this time the cracking capacity of the refining industry increased enormously and most gasoline, whether aviation or motor, contained some cracked constituents. Those companies having natural gasoline plants also included as much natural gasoline as possible.

Since the principal qualification to be met was distillation range, almost any hydrocarbon mixture having the correct distillation qualities was suitable for aviation fuel. Undoubtedly the gasolines from aromatic and naphthenic base crude oils such as California, South Texas, or Venezuela, were premium fuels (as well as benzol blends) because their use apparently resulted in smoother running engines. This was especially true in the water-cooled types.

During this period studies on stability indicated that cracked gasoline blends contained gums or polymers and that the formation of these materials continued in storage. This quality was first recognized by the refiners, and their sales specifications included unsaturation and odor tests before such tests were specified by the users of motor and aviation fuels.

In 1922 government specifications limited the use of cracked gasoline in aviation fuel by establishing a copper-dish gum limit of 3 mg. per 100 cc. and an unsaturation per cent of 1 to 2 per cent, maximum. This almost eliminated cracked gasoline as a blending component for aviation fuel since almost all the unsaturates in cracked naphthas are soluble in concentrated sulfuric acid. Thus, the manufacture of aviation gasoline reverted to fractionating straight-run naphthas or blending straight-run and highly treated cracked naphthas. This situation existed until 1929. Although the unsaturation test was eliminated from the government specifications in 1924, the copper-dish gum limit of 3 mg. was still retained and penalized cracked gasolines. Sulfur content was also limited to 0.10 per cent, maximum, and this caused the adoption of treating methods capable of reducing the sulfur content in both motor and aviation gasolines to below that limit. With the exception of this addition to the refining process, aviation-fuel manufacture still followed essentially the same procedure that it had 10 years previously.

Another thing that should be remembered is that although most of the large commercial users followed the government specifications, this was not universal and probably much of the aviation gasoline sold in 1928 and 1929 was material that would not pass the generally accepted specifications. This allowed quite a variation in quality in the gasoline sold as aviation fuel.

Quantity and Quality of Aviation Fuel Produced to 1929.— From 1903, aviation's first year, until 1918 there was no manufacture of aviation fuel as such. Although gasolines from certain crude oils were more desirable from the user's standpoint, the manufacture of both motor and aircraft gasolines was the same with both the procedure and product being identical. Very little information is available on the quantity of fuel utilized for aviation during this period. From Table 5-I it is evident that the total gasoline production approximately doubled for each 5-year period until 1918. And since the motorcar, bus, and truck

registrations increased in approximately the same proportion, it may be assumed that the amount of gasoline utilized for aviation during this period was relatively small—so small in fact that it probably did not exceed 500,000 gal. for the year 1917.

In 1918, under war conditions, the use of gasoline for aviation purposes increased tremendously over that of previous years. It was mentioned in one source[6] that 750,000 gal. of "fighting grade" aviation gasoline and 2,600,000 gal. of "export grade" aviation fuel were inspected for shipment in a 4-month period in the latter part of 1918. On this basis it would be reasonable to estimate that somewhere around six to eight million gallons were used during that year.

During the First World War undoubtedly a greater portion of the aviation gasoline used was regular motor gasoline ranging from 40 to 60 octane number and having a boiling range between the limits of 100 and 450°F. The "fighting grade" mentioned above probably was 50 to 65 octane number material with a boiling range from 100 to 350°F.

TABLE 5-I.—PRODUCTION OF AVIATION AND TOTAL GASOLINE, 1904–1929*
(Thousands of gallons)

Year	Commercial aviation	Total, all gasoline produced
1904	. . . . . .	290,640
1909	. . . . . .	541,800
1914	. . . . . .	1,466,430
1916	. . . . . .	2,058,882
1918	. . . . . .	2,850,540
1919	. . . . . .	3,570,294
1920	. . . . . .	3,952,870
1926	3,290	10,903,242
1927	5,057	12,588,828
1928	9,899	13,878,270
1929	20,521	15,957,690

* Taken from *Bur. Mines Bull.* 191 (1920); "Petroleum Facts and Figures," 4th and 5th ed., 1931, 1937, A.P.I.

Immediately after the First World War the impetus given to the development of aviation during the war was greatly reduced and the production of airplanes decreased to a minimum. This was primarily due to the fact that military airplane consumption

practically stopped at the end of the war.   Between 1919 and 1929, aviation development and expansion were slow but showed a steady upward trend in the number of machines manufactured and the number of miles flown.   This was attributable to a great extent to the awakening interest of the public in commercial and private flying.   No figures are available on the quantity of aviation fuel manufactured during the period of 1918–1925 since aviation fuel at that time was still apparently considered of insufficient importance to be classed as a special fuel.   In 1926, however, 3,290,000 gal. was reported produced for commercial and private aircraft use.   By 1929, the quantity had increased to 20,521,000 gal.   In addition, government services, including the Army and Navy air forces, probably consumed between ten and fifteen million gallons of aviation gasoline during that year. The average octane number of the fuel was at that time around 65 to 70, while stability, volatility, corrosion, sulfur, and other specifications ensured a fuel of reasonable quality especially adapted to aviation use.

References

1. HILL and DEAN: *Bur. Mines Bull.* 191 (1920).
2. DEAN: *Bur. Mines Tech. Paper* 166 (1917).
3. *U.S. Bur. Mines Tech. Paper* 305 (1922).
4. *Bur. Mines Tech. Paper* 323 (1923).
5. *Bur. Mines Tech. Paper* 323B (1927).
6. *Bur. Mines Bull.* 178C (1919).

CHAPTER II

DEVELOPMENT OF AVIATION FUEL, 1930 TO 1942

Previous to 1930 aviation was in what may be considered its initial stage of development. It was during this time that popular interest in aviation began and private flying became somewhat common. Commercial aviation was being established for passenger, freight, and mail services, and military aviation was advancing rapidly. As a result, by 1930 a great number of air miles were being flown yearly.

In the same manner the fuel requirements began to be sufficiently large to merit more than a cursory interest of the refining industry, and, consequently, attention was turned to aviation gasoline as a special product whose potential value was of no mean importance. It was from this time, around 1930, that the present-day aviation fuel was developed.

Aviation Fuels, 1930 to 1942.—As far back as 1917–1918, Gibson[1] investigated the knocking tendencies of fuels of different types in both air-cooled and liquid-cooled engines. He found that cracked gasoline operated better than a straight-run gasoline in a water-cooled cylinder but was only equal to or worse than straight-run fuel in air-cooled cylinders. Ricardo,[2] and Midgely and Boyd[3] later definitely established the relationship between engine performance and fuel knocking characteristics.

The principal difficulty in specifying a definite antiknock rating for aviation fuels was the lack of a suitable test method. During the 5-year period prior to 1929, a great amount of experimentation was being conducted on this subject and Edgar[4] in 1927 advocated the use of normal heptane and isooctane as tentative reference fuel standards. The standard designation for knocking characteristics of the fuels for a time during this period was the "H.U.C.R." or "H.U.C.P.," the highest useful compression ratio or highest useful compression pressure, of the fuel. This was established as the compression ratio in a given

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engine necessary to produce knocking.   Using the octane scale of Edgar, it was found that the average straight-run aviation gasolines from California crude oils were around 70 and those from Mid-Continent crude oils around 50.   With no specification stabilizing this property, aviation fuels fulfilling all other requirements were furnished to the users with extremely wide variation in octane number.

By the year 1929 it was recognized by most manufacturers and consumers of aviation fuel that some type of antiknock rating must be included in the specifications.   Francis[5] indicated that the antiknock value of a fuel was extremely important in regard to its performance in aviation motors and predicted that the time would come when the chemical composition of the gasoline would have to be known.   He advocated tests on gravity, color, odor, gum content, sulfur, volatility, and antiknock rating to control quality.   Shoemaker[6] stated that antiknock rating was by far the most important basis on which to rate the fuel since the higher antiknock fuels gave increase in usable compression ratio and power.   He also included latent heat, heat of combustion, and volatility as necessary controls of quality.

In 1929 the octane scale was adopted and in 1930 the first octane number specification on aviation fuel appeared.   The U.S. Army Air Forces carried out investigations on comparison of full-scale engine performance with knock-engine tests on aviation fuels and published the results of the investigations in 1930.[7,8]   As a result of this work, the Army Air Forces specified an 87 octane aviation gasoline.   The octane number was determined by special test engine having a 300°F. jacket temperature.

At the time the first octane specification on aviation fuel appeared, the interest of commercial users was divided on five different types of fuels, all having the same general characteristics except for octane number or antiknock rating.[9]   The different types were as follows:

1. U.S. Government domestic grade aviation gasoline.

2. Type 1, plus 2 to 3 cc. of tetraethyl lead per gallon for higher antiknock value.

3. Straight-run gasoline made from a West Coast crude oil having the same antiknock value as Type 2, at a test engine compression ratio of 5.8:1 with a cooling-water temperature of 180°F.

4. Type 1 plus 15 to 20 per cent benzol for higher antiknock value.

5. U.S. Government fighting grade aviation gasoline (329°F., end point).

TABLE 1-II.—AVIATION GASOLINE SPECIFICATIONS, 1935[10,11]

	U.S. Army		U.S. Navy m-222	Commercial range		
	A-2-95	A-2-93		87	80	73
Acid heat, °F., max.			20			
Color, Saybolt, min.	21 (blue)		25 (blue)			
Corrosion, copper dish............	None	None	None	None	None	None
Distillation, % recovery:						
10%, °F., max....	167	158	167		158–167	
50%, °F., max....	212	230	212		194–221	
90%, °F., max....	275	320	275		230–311	
10+50%, °F., min.	307	307				
Recovery, %, min.	96.0	96.0				
Residue, %, max.	2.0	2.0	2.0			
Acidity of residue.	None	None	None	None	None	None
Freezing point, °F., max.............	−76	−76	−76	−76	−76	−76
Gum, accelerated, mg./100 cc., max.	10		10	10	10	10
Gum, copper dish, mg./100 cc., max.		3.0				
Octane number, min.	92*	65	87, 83, 80, 73	87	80	73
Sulfur, %, max.....	0.10	0.10	0.10	0.10	0.10	0.10
Tetraethyl lead, cc./ gal., max.........	6.0		5.0	2.0	3.0	3.0
Vapor pressure Reid, lb., max....	7.0	7.0	7.0		7.0–7.5	
Water tolerance, max.............	±2 ml.	±2 ml.				
Water and sediment.	None	None	None	None	None	None

* C.F.R. method (modified: 1,200 r.p.m.; cylinder, 2⅝ in.; jacket temperature, 330°F.; and thermal plug for maximum knock determination).

All the gasoline types except Type 5 had the same distillation range and other characteristics except for antiknock value and the means of obtaining it (blending with tetraethyl lead or benzol

and selection of crude base).   Type 5 differed in distillation range in that it had an end point of 329°F. while the others had end points of 374°F.

From 1930 to 1934, interest in aviation fuel quality increased greatly.   A great amount of investigation was carried out on antiknock test methods and correlation of performance with laboratory test data.   Also, during this period additional tests appeared which further increased control of quality in relation to performance demands.   These were the accelerated aging test, vapor-pressure test, freezing-point test, and acid heat test. The 10 per cent point in the distillation range was established as the point indicating volatility, and in most cases the volume per cent points in the distillation were changed from per cent recovered to per cent evaporated.   Benzol additions were limited to 20 per cent or less (because of its high freezing point) and the amount of treated cracked gasoline allowed in the blend was somewhat limited.

By 1935 there were seven different aviation-fuel specifications based on octane rating.   There were two Army grades, four Navy grades, and three commercial grades, and some of these were comparable on the basis of octane rating.   The 92 octane Army grade was very similar to the 87 octane grade of the Navy and commercial specifications [87 octane number by the Motor method corresponds to about 92 octane number with the modified C.F.R. (Cooperative Fuel Research Committee) method using the thermal plug to determine maximum knock].

The Army 92 grade and Navy grades were identical with respect to distillation range and certain other tests with the exception of acid heat, maximum allowable tetraethyl lead content, and water tolerance.   The commercial grades differed in distillation range, vapor pressure, and tetraethyl lead content. No acid heat or water tolerance specifications were generally established by commercial users.

The number of grades specified showed a lack of agreement among various aviation fuel users as to the qualities necessary in an aviation gasoline.   This was due in part to insufficient data on correlation of laboratory tests with actual performance. By 1937 this confusion had led to the establishment of 14 different aviation-fuel specifications in this country based on antiknock value and 11 in foreign countries.

TABLE 2-II.—AVIATION FUEL SPECIFICATIONS, 1937[12]

Grades (octane)

Property	U.S. Army			U.S. Navy					Commercial					
	100	92	65	100	87	83	80	73	95	93	90	87	80	74
Acid heat, °F, max				20	20	20	20	20			20–40†			
Calorific value, B.t.u./lb., min	20,500 on any fuel								20,500 on some 95 and 90 grades					
Corrosion, copper dish	No corrosion permitted for any fuel													
Distillation:														
5%, °F, max										150			140–150	
10%, °F, max	167	167	158	167	167	167	167	167	167	167	167		150–167	
50%, °F, max	212	212	230	212	212	212	212	212	212	212	212		195–221	
90%, °F, max	275	275	320	275	275	275	275	275	275	266	275		231–347	
96%, °F, max	307									311			252–275	
10% + 50% °F, min	307	307	307	307	307	307	307	307	307	307	307	307	307	307
Recovery, %, min										96.0	1.0	96	96	96
Residue, %, max	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.0–2.0	2.0
Loss, %, max										2.0	2.0		2.0	
Freezing point, °F, max	-76	-76	-76	-76	-76	-76	-76	-76	-76	-76	-76	-76	-76	-76
Gum, accelerated, mg./100 cc., max	10.0	10.0		10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Octane number (min.)	100*	92*	65*	100*	87	83	80	73	95	93	90	87	80	74
Sulfur, %, max	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Tetraethyl lead, cc./gal., max	3.0	6.0	0	3.0	0.5–3.27	2.29	1.63	0	4.0	3.0	4.0	2–3	1.1–2	0
Vapor pressure, Reid, max	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0–7.5	7.0–7.5	7.5

NOTE: All octane numbers determined by C.F.R. Motor method unless marked *.

* Octane number determined by Army method.

† Nitration acid heat test.

Hubner *et al.*[12] published these specifications and discussed them from the standpoint of possible standardization and reduction of the number of grades required.   Table 2-II shows the different types of aviation fuel required in 1937.

The principal change in the status of specifications from 1935 to 1937 was the adoption of 100 octane grades by both the Army and Navy and the adoption of 90+ octane grades by a number of commercial users.   Thus, a definite tendency toward higher octane number fuels began to be evidenced by aviation in general.

TABLE 3-II.—AVIATION-FUEL SPECIFICATIONS 1939[13]
(Commercial)

	Grades				
	95	90	87	80	73
Acid heat, °F., max............	15	15	15	15	15
Calorific value, B.t.u./lb., min..	19,000	19,000	19,000	19,000	19,000
Distillation:					
10%, °F., max..............	158	158	158	158	158
50%, °F., max..............	212	212	212	212	212
90%, °F., max..............	257	257	257	257	257
10% + 50%, °F., min.......	307	307	307	307	307
Freezing point, °F., max........	−76	−76	−76	−76	−76
Gum, accelerated, mg./100 cc., max......................	6	6	6		
Octane number (Motor), min....	95	90	87	80	73
Sulfur, %, max...............	0.10|	0.10|	0.10	0.10	0.10
Tetraethyl lead, cc./gal.:					
Max......................	4.0	4.0	3.0	2.0	
Min......................	3.5	3.5			
Vapor pressure, Reid, max......	7.0	7.0	7.0	7.0	7.0

Although a great number of octane grades were specified at this time, the other important properties desired and specified in aviation fuels were as a whole comparable.   A great many differences existed in the octane number specifications because very little reliable information was available concerning correlation of performance data with test-engine data.   The Cooperative Fuel Research Committee undertook the study of antiknock methods in relation to fuel performance and, through their efforts, conferences between commercial aviation fuel users and

producers in 1938 resulted in simplified specifications for five different fuels. Table 3-II lists these specifications.

The Army and the Navy standardized their requirements at that time, specifying six different fuels with four octane grades. Three were unleaded gasolines. There were three distillation requirements all having higher 90 per cent points and three having higher 50 per cent points than were permitted in commercial specifications.[13]

This unification of specified types of fuels by both the government services and commercial users resulted in over-all requirements of essentially five different grades. The Army and the Navy could use aviation gasolines produced to meet the commercial specifications but, because of the wider government limits, not always could commercial aviation use the fuel produced according to government specifications.

With the number of fuels specified reduced to approximately five, the situation of the refiner was much improved over the previous year (1937) when 14 noninterchangeable grades had to be stocked. However, owing to increased consumption of aviation fuels, it was recognized that further simplification was necessary to ensure adequate supplies of gasoline.

By 1941, principally through the efforts of the Cooperative Fuel Research Committee, the number of commercial grades of aviation fuel required were reduced to three. These were 73, 91, and 100 octane number. This was the result of studies of test-engine data and correlation of full-scale engine performance of fuels ranging from 90 to 100 octane number. A new method[14] of rating antiknock qualities of aviation fuels was developed from these studies and appears to be more satisfactory than others previously developed in indicating fuel quality in actual full-scale engine performance.

The specifications for the three grades of fuels required by commercial users are given in Table 4-II.

A comparison of the 1939 commercial specifications with those of 1942 shows three octane grades required instead of five. The calorific values of all grades were lowered, the acid heat test was eliminated, the maximum permissible total sulfur content was cut in half, and the highest octane grade required was 100 instead of 95. In addition, the antiknock values were determined by the new A.S.T.M.-C.F.R. Aviation method.

It is not permitted to publish Army and Navy aviation-fuel specifications, owing to war restrictions, but it is permissible to say that they are somewhat similar to the commercial specifications.

Aviation-fuel Manufacturing Methods, 1930 to 1942.—From 1930 to 1938, owing to the ever-increasing number of different specified aviation-fuel types, large refining companies that were

TABLE 4-II.—AVIATION-FUEL SPECIFICATIONS, 1942[15]
(Commercial)

	Grades		
	100	91	73
Calorific value, net, B.t.u./lb., min........	18,700	18,700	18,300
Color................................	Blue	Blue	Blue
Corrosion, copper dish.................	None	None	None
Corrosion, copper strip.................	None	None	None
Distillation:			
10%, °F., max......................	158	158	158
50%, °F., max......................	212	212	212
90%, °F., max......................	257	257	257
10% + 50%, °F., min...............	307	307	307
Recovery, %, min...................	97.0	97.0	97.0
Residue, %, max....................	1.5	1.5	1.5
Loss, %, max......................	1.5	1.5	1.5
Acidity of residue....................	None	None	None
Freezing point, °F., max.................	−76	−76	−76
Gum, accelerated, mg./100 cc., max.......	6	6	6
Gum, copper dish, mg./100 cc., max......	5	5	5
Octane number,[14] min..................	100	91	73
Sulfur, %, max........................	0.05	0.05	0.05
Tetraethyl lead, cc./gal., max............	3.0	4.0	1.0

attempting to supply both government service and commercial markets were unable to concentrate their efforts on any one type of fuel. Some companies were required to stock no less than 14 grades of aviation fuel, all sufficiently different from one another to prevent substitution. This situation was not particularly conducive toward development from the refiners' standpoint. After standardization of the commercial specifications reduced the number of grades to five in 1938 and later to three in 1941, the refining industry was able to concentrate on con-

version process manufacture of high-antiknock fuels, and added impetus was given to the establishment of large capacity facilities for such manufacture.

Aviation-fuel manufacturing methods began to change radically around 1930 owing to the recognition of users and manufacturers of the importance of knocking or detonation in engines caused by fuels of improper quality. Investigatory work had resulted in the acceptance of several facts in connection with the performance of aviation fuels in regard to knocking or detonation characteristics:

1. Tetraethyl lead, developed in the early twenties, was a satisfactory antiknock "dope" or addition agent for use in normal aviation gasolines.

2. Hydrocarbon structure was extremely important in relation to antiknock quality of fuels. It was found that the straight-chain paraffins in the gasoline boiling range had low-antiknock values and the isoparaffins had high-antiknock values. Also, the olefins, the lower molecular-weight cycloparaffins, and aromatics in general all had high-antiknock values.

3. Knocking fuels gave much lower motor efficiencies than nonknocking fuels and in many cases had destructive effects on the motors themselves.

With the establishment of an 87 octane fuel specification by the Army Air Forces and the alignment of many of the commercial users with this requirement, the attention of the refining industry was directed toward new and satisfactory methods of manufacturing such a fuel. Previous to this time, distillation requirement was the most important characteristic to be met, and the average antiknock value was approximately 50 (octane number).

Because of other limitations imposed in government service and commercial specifications in regard to freezing point, gum stability, vapor pressure, unsaturation (acid heat), and maximum tetraethyl lead content, the production of suitable antiknock fuels was limited to certain methods. These were in general as follows:

1. Production of a straight-run gasoline of required characteristics and "leading" to the required octane number.

2. Addition of limited amounts of benzol (below 20 per cent) to a straight-run gasoline for antiknock requirements.

3. Fractionation of select naphthas and natural gasolines and addition of limited amounts of high-vapor-pressure hydrocarbons having high-antiknock values.

4. Manufacture of pure hydrocarbons or hydrocarbon mixtures having extremely high-antiknock values and addition of these to a base stock with or without tetraethyl lead to achieve the correct antiknock value in the blended fuel.

TABLE 5-II.—PRODUCTION OF AVIATION AND TOTAL GASOLINE, 1930–1942*
(Thousands of gallons)

Year	Aviation			Total gasoline produced
	Commercial	Government	Total	
1930	28,531	......	....	18,273,276
1931	30,815	......	....	18,321,114
1932	33,981	20,078	54,059	18,123,420
1933	35,188	21,836	57,024	16,490,166
1934	34,167	23,647	57,814	16,866,822
1935	44,365	29,319	73,684	17,511,144
1936	47,509	31,758	79,267	19,229,364
1937	52,043	36,209	88,252	19,501,618
1938	55,511	44,937	100,448	19,600,000
1939	72,331	......	132,500	23,000,000‡
1940	96,935	......	225,456	24,335,190‡
1941	......	......	613,200†	25,000,000‡

* From "Petroleum Facts and Figures," 6th and 7th eds., 1939 and 1941, A.P.I. Ethyl Gasoline Corp.[19]

† Estimated 100 octane production.

‡ Estimated.

For a time until around 1935–1936, the first three methods of aviation fuel manufacture were sufficient for general purposes. Meanwhile, intensive research was being carried out by many petroleum refining research organizations on the fourth method. As the result of this research new methods for the production of isooctane appeared, such as polymerization and alkylation and the supplementary processes of dehydrogenation, hydrogenation, and isomerization.

In another direction but with the same end in view, processes were developed for the production of large quantities of high-octane base stocks through conversion methods that were

suitable for motor gasoline or aviation gasoline.   These were catalytic cracking, hydroforming or aromatization, gas reversion or polyforming, and naphtha isomerization.   Such processes give base stocks ranging in octane number from 75 to 85 which normally require some additional treatment before utilization as aviation fuels and aviation-fuel bases.

With the advent of 100 octane aviation-fuel requirements, such processes are vitally necessary.   Gasoline produced in such a manner is more expensive than that produced by the older methods but, from a performance standpoint in efficiency and economy, the additional cost is more than justified.   At the present time the petroleum industry is utilizing such conversion

TABLE 6-II.—COMPARISON OF AVERAGE OCTANE REQUIREMENT OF ARMY
AND COMMERCIAL AVIATION[16]

(Average octane number weighted on gallonage basis)

	Army	Commercial
1932	82	73
1933	87	79
1934	90	80
1935	91	83*
1936	93	85*
1937	95	87*
1938	98*	89*

* Estimated.

methods almost exclusively for the production of the higher grades of aviation fuel.

Aviation-fuel Quantity and Quality, 1930–1942.—Upon the adoption of antiknock ratings on aviation fuels in 1930, the Army specified 87 octane (Army Method) aviation gasoline as a "first-line" fuel.   At the same time the average commercial gasoline was around 70.   By 1935 the first-line or "fighting" grade demanded by the Army was 100 octane number while the commercial demands were for the 87 octane grade.   The weighted average octane number of all aviation fuel used by the Army in 1935 was 91 and that used by the commercial companies was approximately 83.

Table 6-II compares the commercial demand and the Army demand in regard to the average octane number of all fuels used

(weighted on a gallonage basis).   Until recently the commercial octane number demands have been somewhat less than that of the Army.   By 1938, 98 octane number fuel was used by the Army and 89 by commercial users.

TABLE 7-II.—CONSUMPTION OF AVIATION FUEL BY U.S. ARMY AIR FORCES BY OCTANE NUMBER[17]

(Thousands of gallons)

	Grades					Total consumption all grades
	65	87	92	92*	100	
1932	1,500	9,200	......	...	....	10,700
1933	1,000	5,300	7,000	...	....	12,300
1934	600	.....	13,300	...	....	13,900
1935	550	.....	16,300	...	270	17,125
1936	650	.....	15,350	170	2,580	18,750
1937	700	.....	14,450	485	6,230	21,865
1938	1,200	.....	9,000	700	∴ 15,000	25,900
1938–1939	.....	.....	......	...	20,000–25,000	
1939–1940	966	.....	2,039	588	27,349	30,942

* Unleaded.

TABLE 8-II.—PER CENT REQUIREMENTS OF U.S. ARMY AIR FORCES FOR VARIOUS OCTANE NUMBERS[18,16]

	Octane number				Average octane
	58–65	87	92	100	
1930	56.4	43.6	.....	....	70.6
1931	31.6	68.4	.....	....	77.7
1932	16.6	83.4	.....	....	82.2
1933	6.5	50.2	43.3	....	87.3
1934	5.3	....	94.7	∴.....	90.2
1935	3.9	....	91.7	4.4	91.3
1936	3.5	....	77.5	19.0	92.6
1937	3.0	....	68.0*	29.0	93.3
1938†	3.0	....	7.0	90.0	98.2

* 2.0 per cent, 92 octane, unleaded.
† Estimated.

An interesting comparison of the quantities of various octane-grade aviation fuels used by the Army is found in Tables 7-II and 8-II.   In 1932, 1,500,000 gal. of 65 octane fuel representing

16.6 per cent of total fuel requirements, and 9,200,000 gal. of 87 octane fuel representing 83.4 per cent of the total requirement were used. In 1935, 100 octane fuel made its appearance in commercial quantities, and 270,000 gal., or 4.4 per cent, of the total Army requirement was that grade while 91.7 per cent was 92 octane fuel.

By 1940, 27,000,000 gal. of 100 octane fuel representing 90 per cent of its requirement was used by the Army Air Forces.

The total consumption of aviation fuels of all grades increased from 54 million gallons in 1932 to approximately 225 million gallons in 1940. The jump in consumption from 132 million gallons in 1939 was due to the war demands. Rough estimates[19] of the quantity of aviation fuel produced in 1941 were around 700 million gallons and for 1942 around 2 to 2.5 billion, most of which is the 100 octane grade. By far the greater proportion of this was used for military purposes.

Since the beginning of the Second World War and particularly since the entrance of this country into the conflict, aviation-fuel production has skyrocketed. Not only has the quantity increased but also the quality. With 100 octane aviation fuel composing the greater portion of the fuel produced, at the end of the war the facilities of the refining industry should be able to supply sufficient 100 octane fuel for all commercial and military needs and still allow for the inevitable expansion of aviation in all fields.

In addition, fuels having octane numbers above 100 are being considered. Owing to the enormous increase in power, efficiency, and economy effected by the use of fuels having octane numbers of 100 plus, it is reasonable that eventually such materials will be produced for general use. The research organizations of the refining industry are studying this problem and are expected to solve it in the usual satisfactory manner.

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SPECIFICATIONS AND TEST METHODS
ON AVIATION FUELS

In Chap. I it was shown that, before the year 1930, the specifications for aviation fuel were few and somewhat general in nature. Until that time no antiknock specification had been established by the users and producers of the fuel other than a general one designated as "high-test." This required that the gasoline be of high A.P.I. gravity and was based on the observation that the higher A.P.I. gravity fuels in general gave less audible knock in operation in engines.

Upon development of a suitable antiknock rating method which was effective in rating fuels in the laboratory, antiknock specifications appeared and are today one of the principal control specifications on aviation fuel. With the general acceptance of antiknock rating methods, by 1937 there were 14 different aviation-fuel specifications in use in this country based on this rating. The number dropped to 11 in 1939 and to 4 in 1941, and undoubtedly the problem of supply under war conditions will further reduce the number of octane grades specified.

SPECIFICATIONS FOR AVIATION FUELS

Aviation-fuel specifications in general must fulfill several purposes. First of all, they should be devised to give satisfactory operation of the engines in which the fuels are to be used. This is by far the most important purpose from an engineering or technical standpoint, and from that standpoint this is the only real function of specifications.

From the practical economic side there are other considerations that must be made in regard to cost and availability. It is conceivable that a pure hydrocarbon compound would give the most satisfactory performance in an engine of special design and therefore, on the basis of engineering, this compound of a given degree of purity would be specified. However, its manu-

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facturing cost might be $1,000 per gallon and this factor would naturally prevent its use. It is evident then that specifications should take into account the economic angle involved in the cost of fuel manufacture and, coincidentally, the cost of the fuel to the user.

Another important consideration is that of supply. Specifications should be written so that the fuel under consideration will be available in sufficient quantity for the users' needs. This is more important now than ever before because of the enormous growth of aviation in the last few years. In 1937, fourteen different octane grades were specified by government and commercial users; by 1941 there were essentially four grades with only slight variations in certain of the specifications. This reduction in number of specified grades and standardization of specifications is mainly due to the economic factor of availability of supply.

The Aviation Fuels Division of the C.F.R. Committee and the A.S.T.M., both societies representing cooperative effort of fuel manufacturers and users, have done much toward the standardization of aviation gasoline specifications. The government services have also cooperated in this effort.

Table 1-III lists the A.S.T.M. tentative aviation-fuel specifications for 1942 and also, approximately, the ranges of specifications covering aviation fuels in general.

Under present conditions it is not permissible to publish the specifications issued by the Army and the Navy on aviation fuel, but it is possible to say that they are somewhat of the same order as the commercial specifications. In addition to the 100, 91, and 73 octane grades, the government agencies also specify a 65 octane (unleaded) gasoline.[1]

From Table 1-III we find that the important properties necessary in aviation gasoline are as follows:

1. Required antiknock values.
2. Correct volatility and vapor pressure.
3. Stability in use and storage.
4. Noncorrosiveness.
5. Extremely low freezing point.
6. Correct thermal properties (low latent heat, high heat of combustion).
7. Minimum water solubility.
8. Good lead susceptibility.

TABLE 1-III.—SPECIFICATIONS ON AVIATION FUEL

	A.S.T.M.—tentative[2]			Range		
	Grade			Grade		
	73	91	100	73	91	100
Acid heat, °F., max						
Calorific value, net, B.t.u./lb., min	18,300	18,700	18,700	18,000–18,500	18,500–18,700	18,500–18,700
Color, Saybolt, min	Blue	Blue	Blue	Blue	Blue	Blue
Corrosion, copper dish	None	None	None	None	None	None
Corrosion, copper strip	None	None	None	None	None	None
Distillation, A.S.T.M.:						
10% evaporated, °F., max	158	158	158	158–168	158–168	158–168
50% evaporated, °F., max	212	212	212	212–221	212	212
90% evaporated, °F., max	257	257	257	257–300	257–275	257–275
10% + 50% evaporated, °F., min	307	307	307	307	307	307
Recovery, %, min	97.0	97.0	97.0	97.0	97.0	97.0
Residue, %, max	1.5	1.5	1.5	1.5	1.5	1.5
Loss, %, max	1.5	1.5	1.5	1.5	1.5	1.5
Acidity of residue	None	None	None	None	None	None
Freezing point, °F	−76	−76	−76	−76	−76	−76
Gravity, A.P.I.	*	*	*	*	*	*
Gum, accelerated, mg./100 ml., max	6.0	6.0	6.0	5.0–6.0	5.0–6.0	5.0–6.0
Gum inhibitor, lb./5,000 gal., max	1.0‡	1.0		0–1.0	0–1.0	0–1.0
Octane number, min.§	73	91	100	73	91	100
Sulfur, %, max	0.05	0.05	0.05	0.05–0.10	0.05–0.10	0.05–0.10
Tetraethyl lead, cc./gal., max	1.0	4.0	3.0	1.0	4.0	3.0–4.0
Vapor pressure, Reid, max	7.0	7.0	7.0	7.0	7.0	7.0
Water miscibility, max	±2 ml.†	±2 ml.†	±2 ml.†	0–±2 ml.†	0–±2 ml.†	0–±2 ml.†

* Not specified but usually reported.
† Volume change not to exceed 2 ml.
‡ Permissible gum inhibitors:
 Monobenzyl-p-aminophenol
 Isobutyl-p-aminophenol
 n-Butyl-p-aminophenol
 n, n^1-Dibutyl-p-aminophenol
 o-, m-, and p-Cresols
 α-Naphthol
§ A.S.T.M.-C.F.R. Aviation method.

TEST METHODS AND THEIR VALUE IN RATING AVIATION FUELS

Coincident with the improvements in the design of airplane motors, the quality of fuels to be utilized in them was also improved. As fuel quality improved, new specifications appeared which resulted in new, more sensitive, and more accurate test methods. These are grouped in two general classifications: laboratory tests and performance tests. Performance tests are extremely valuable and, as we shall see later, the only absolute means of determining certain characteristics of the fuels. However, these are expensive and time consuming, and in most cases it is impossible for the fuel manufacturer, particularly, to run performance tests on his product. As a result, laboratory test methods are used almost exclusively by refiners to determine the characteristics of aviation fuels. These are standardized and, in many cases, the results obtained are capable of being correlated with actual performance data.

Laboratory methods used in the characterization of aviation fuels may be grouped as follows:

<div align="center">AVIATION-FUEL TESTS*</div>

1. Antiknock value
   a. A.S.T.M.-C.F.R. Motor method
   b. C.F.R. Research method
   c. A.S.T.M.-C.F.R. Aviation method
   d. U.S. Army method
   e. British Air Ministry method
2. Color
   a. Saybolt Color method
3. Low-temperature Properties
   a. Freezing-point test
4. Stability—oxidation resistance
   a. Gum—air-evaporation method
   b. Copper-dish gum test
   c. Oxygen-bomb test—induction period
   d. Accelerated gum test
   e. Acid heat test
   f. Modified acid heat test
5. Corrosion properties—sulfur content
   a. Lamp sulfur determination
   b. Copper-strip corrosion
6. Vaporization characteristics
   a. Distillation
   b. Reid vapor pressure

* The test methods listed are described briefly in the Appendix.

Antiknock Properties.—Antiknock values are specified for the various grades of fuels because it has been established that fuel knock (either audible or that evidenced by temperature rise in the cylinder) in an ignition internal-combustion type motor lowers its operating efficiency and has destructive effects on the motor itself. For a given engine design, made to operate at a set compression ratio, it is necessary to have a fuel of defined minimum antiknock value to ensure safe and efficient operation. Because of the failure of antiknock testing methods to evaluate fuels for all motors on the basis of performance under operating conditions, experience and actual correlation of performance in a particular design of engine with test method results are important in establishing the correct specification. Improvements are constantly being made in antiknock rating methods and it is hoped that in the near future performance values and laboratory test values will be strictly and definitely comparable.

Antiknock value for motor and aviation fuels is determined in the United States by one of several methods, each of which uses conditions of operation or equipment slightly different from the others and, therefore, usually gives a different antiknock rating to the same fuel. Four American methods and one British test method are commonly used. These are the A.S.T.M.-C.F.R. Motor method, C.F.R. Research method, A.S.T.M.—C.F.R. Aviation method, U.S. Army method, and the British Air Ministry method. Differences in operating conditions are listed in Table 2-III, and the procedures are discussed under the different tests described in the Appendix.

Significance of Antiknock Rating Methods.—When it was first recognized that antiknock value of fuels was an important characteristic in the operation of internal-combustion engines, it was believed that fuels giving a definite knock rating in one test engine should have the same rating in all engines. This was soon found to be a false belief, and information was obtained that showed that the knocking tendency of a particular fuel varied with engine speed, mixture temperature, compression pressure, any many other related variables. Cooperative research among various test standardization societies, the engine manufacturers, the petroleum industry, and government services, has done much toward the development of methods which give uniform antiknock ratings to aviation and motor fuels and which give values

TABLE 2-III.—OPERATING CONDITIONS OF ANTIKNOCK TEST METHODS

	A.S.T.M.-C.F.R. Motor method	A.S.T.M.-C.F.R. Aviation method	U.S. Army method (until January, 1941)	C.F.R. Research method (1939)	British Air Ministry method
Speed	Constant, 900 r.p.m. ± 9 r.p.m.	Constant, 1,200 r.p.m. ± 12 r.p.m.	Constant, 1,200 r.p.m. ± 20 r.p.m.	Constant, 600 r.p.m. ± 6 r.p.m.	Constant, 900 r.p.m. ± 9 r.p.m.
Jacket temperature (coolant temperature)	209°F.–215°F., constant ± 1°F, throughout test	374°F. ± 9°F.	330°F. ± 5°F., constant ± 2°F. throughout test	209°F.–215°F., constant ± 1°F, throughout test	209°F.–215°F., constant ± 1°F, throughout test
Mixture temperature	300°F. ± 2°F.	220°F. ± 2°F.	Room temperature (100°F.)	125°F. ± 2°F.	
Air-intake temperature	....	125°F. ± 5°F.	....		
Spark advance	Automatic, 26.0° at 5:1 compression ratio (base)	Constant, advanced 35° ± 1° for all compression ratios	Constant, advanced 30° for all compression ratios	Constant, advanced 13.0° for all compression ratios	Automatic, 26.0° at 5:1 compression ratio (base)
Fuel blends for checking engine	65% isooctane, 35% n-heptane (at 5.3:1 compression ratio)	87% isooctane, 13% n-heptane matched against c.p. benzene to give same thermal-plug temperature	88% isooctane, 12% n-heptane matched against c.p. benzene to give same thermal-plug temperature	70% isooctane, 30% n-heptane (at 5.75:1 compression ratio)	65% isooctane + 35% n-heptane (at 5.3:1 compression ratio)
Instruments for knock indication	Bouncing pin and knockmeter	Thermal plug	Thermal plug	Bouncing pin and knockmeter	Bouncing pin and knockmeter

somewhat comparable to those obtained from full-scale engine performance. However, much yet remains to be done in this field since not only do the methods used at present give somewhat widely varying results for fuels of different types, but also do not rate them too satisfactorily on the basis of full-scale engine performance.

In 1938, Heron and Beatty[3] reported on the characteristics of the methods used at that time and listed the following conclusions:

1. The A.S.T.M.-C.F.R. Motor method rated satisfactorily different types of straight-run gasolines, clear and leaded; cracked gasolines, clear and leaded; and benzol-straight-run unleaded gasolines within the range of 70 to 83 octane number. It underrated, by 6 to 8 octane numbers, straight-run leaded gasolines of above 87 octane number. Blends of isooctane with straight-run gasoline and 3 cc. of tetraethyl lead were rated around 4 octane numbers lower. Eighty-seven octane number benzol blends were overrated in some cases and underrated in others as much as 8 octane numbers.

2. The C.F.R. Research method rated aromatic blends and cracked or unsaturated gasolines much higher than the A.S.T.M. Motor method.

3. The Army method gave ratings for straight-run gasolines, clear and leaded; cracked gasolines, clear and leaded; and benzol straight-run gasoline blends of 80 octane number or less comparable to those obtained from the Motor method. Above 80 octane number the difference in rating between the two methods became greater the higher the octane number. An 87 A.S.T.M. Motor octane number (gasoline containing 2 to 3 cc. of lead) would equal 90 to 92 octane number when rated by the Army method. The Army method underrated leaded gasolines of around 102 full-scale engine octane number by 2 or more octane numbers. Benzol blends of above 87 octane number were underrated and overrated in different cases by the Army method.

4. The British Air Ministry method rated cracked and aromatic fuels in general slightly higher than the A.S.T.M. method. Leaded gasolines of 87 octane number may be rated higher or lower.

These methods were not entirely satisfactory for the following reasons:[3]

1. They were not sufficiently sensitive to change in octane number above, and around, 100.

2. In general, they were not sensitive to highly leaded gasoline octane numbers.

3. Aromatic type fuels were generally underrated.

These conclusions were based on observation of full-scale engine performance.

Supercharging test methods are able to rate high-octane fuels more satisfactorily than others even though new and improved nonsupercharging methods have been devised, although as late as 1939 they were considered[4] costly, complicated, and slow, and were not supported by sufficient experimental data to make possible the devising of a standard method. Owing to recent developments, certain of the disadvantages have been overcome and supercharging test methods are being widely used by both aviation-fuel users and manufacturers.

In testing fuels of high antiknock rating by laboratory test-engine methods, different considerations must be made for motor fuel and for aviation fuel. In an automobile engine the principal consideration is audible knock caused by preignition detonation and preignition without audible knock is of no great importance. In the case of aviation high-output engines, pre-ignition usually causes very destructive cylinder effects in a short time. Aromatics and completely olefinic fuels may not produce audible knock in aviation engines but through preignition can cause destructive engine effects due to overheating[3] of the piston and cylinder wall. Thus it is indicated that other means than determination of audible knock of aviation fuels must be resorted to to get a true fuel performance picture.

In view of this an agreement has been reached that the lowest performance octane rating of a given fuel in a multiple-cylinder engine will be accepted as the octane number. For example, if a fuel is rated at 80 octane number in one engine and 90 in another, 80 will be the accepted rating.

Color.—Color of aviation fuels is determined by means of the Saybolt chromometer when the fuel is undyed. The color of dyed fuel is determined by comparison with color standards.

At one time, the color of a gasoline was relatively important since it indicated roughly its degree of refining. In stored fuels, color changes were indicative of their stability. Since the advent of "leading" and dyeing, Saybolt colors are of little value except for color evaluation of unblended base stocks. Most aviation

fuels are dyed to serve as identification or to compensate for undesirable colors caused by the use of addition agents.

Low-temperature Properties.—The most important low-temperature property of aviation gasoline is that of the freezing point or the temperature at which crystallization of one or more of its components occurs. In high-altitude flying the temperatures encountered may be lower than $-100°F$. After exposure of the fuel to such temperatures for extended periods of time, as in cruising operations, the fuel temperature approaches that of the atmosphere.

The freezing point established as a general specification is $-76°F$., which is usually sufficiently low to protect aircraft flying at high altitudes. Since the average atmospheric temperature decrease is $3.6°F$. per 1,000-ft. increase in altitude,[5] at 40,000 ft. the atmospheric temperature would be around $-70°F$. Under these conditions the atmospheric temperature is approaching the freezing-point specification limit of the gasoline. However, with few exceptions, the freezing point of the average aviation fuel is actually much lower than the specification, so the problem is not so serious as it appears.

Presence of hydrocarbons that have high freezing points, such as benzene (f.p. = $42°F$.), in certain fuels causes high freezing points of the fuels. Aromatic-type compounds also dissolve about 10 times[3] as much water as do normal gasolines. According to Bass[6] these undesirable characteristics limit the maximum amount of benzol contained in an aviation fuel to around 20 per cent for $-60°F$. freezing point. For a $-76°F$. freezing point this percentage is somewhat lessened. Substituted aromatics such as toluene, xylene, or cumene, have satisfactorily low freezing points.

Stability.—Stability specifications are designed for the purpose of securing fuels that can be stored for reasonable periods of time without excessive gum formation due to oxidation of unstable components. Likewise, fuels containing more than a minimum of gums and polymers that cause undesirable engine deposits are eliminated by these specifications. As in the evaluation of other properties, exact correlation between test results and actual performance is extremely difficult. However, experience has enabled the users of aviation fuel to arrive at a reasonably safe

limit in specifying maximum gum formed under test conditions and these appear as limits in Table 1-III.

Use of the acid heat tests to determine the amount of unsaturated materials present in a motor fuel, thus indirectly indicating stability, has not been very satisfactory. The fault of this type of test is that it indicates total unsaturation and many types of unsaturated compounds are relatively stable under storage conditions and do not cause gum formation.

Several test methods have been developed for evaluating the stability of aviation gasolines (and others). Some are designed for the specific determination of gum- and polymer-forming tendencies directly and have been correlated to some extent with the actual stability of the fuels in storage and under operating conditions. Others are indirect tests in that they indicate roughly the type and amount of unstable hydrocarbons in the fuel. These tests are of less value for stability evaluation than for hydrocarbon-type determination.

The classifications of the two different test types are given as follows:

Gum-formation and Stability Tests
1. A.S.T.M. air-evaporation test
2. Copper-dish gum test
3. A.S.T.M. induction-period test
4. Accelerated gum test

Hydrocarbon-type Tests
1. A.S.T.M. acid heat test
2. Modified acid heat test (nitration)

Significance of Gum and Stability Tests.—The air-evaporation and copper-dish gum tests indicate the amount of gum in the gasoline at the time of the test. Probably it would be more accurate to say that they indicate the amount of gum present plus the amount capable of being formed under the conditions of the test. It is conceivable that the diolefins might easily polymerize to form gum or polymer when heated, and particularly when heated in the presence of copper as in the case of the copper-dish test.

Much work has been done in the past to correlate engine deposits with the results secured from gum tests. Aside from the fact

that gasolines having higher gum contents as determined by laboratory tests cause more engine deposits than those having lower gum contents, no definite conclusions have been reached. Therefore, the tolerance or maximum allowable gum content according to laboratory test is somewhat arbitrary and is based on experience.

The copper-dish test is also valuable in indicating the presence of corrosive materials in the fuel. The presence of sulfur or sulfur compounds is indicated by a black or gray discoloration; the presence of acidic materials is shown by other discolorations.

The oxygen-bomb tests indicate to a certain degree the tendency of a gasoline to form gum in storage due to oxidation. Pressure accelerates both oxidation and polymerization of the gasoline constituents. The gums formed are acidic, resinous materials containing aldehydes and peroxides.

The type of hydrocarbons contained in a gasoline is an important factor in its gumming tendency. It has been shown[7,8] that the monoolefins show no gum-forming tendencies by themselves and the diolefins and cycloolefins are generally considered to be the materials that form gum readily. Also, the olefin-substituted aromatics show this property.

Oxygen-bomb tests have been studied from the standpoint of correlation of induction period with actual storage behavior. It can be said generally that a long-induction-period gasoline will have less tendency to form gum in storage than one with a short induction period. The actual correlation has not been definitely established. This is due in part to the fact that the temperature used in the bomb test is much higher than that encountered in storage, and differences in temperature affect the behavior of the reactions. Reasonable prediction of the behavior of gasoline in storage from results of bomb tests is possible only when storage tests on similar gasolines have been correlated with the laboratory method.

The use of the iron catalyst in the accelerated bomb test serves to catalyze the oxidation reaction. As to the correlation of the results with actual behavior of the gasoline in storage, the foregoing statements hold true.

Different authorities, in attempting to correlate laboratory results with performance, differ in their conclusions as to the maximum amounts allowable. Seven to 15 mg. of gum per 100 cc. by the evaporation method, 15 to 25 mg. per 100 cc. by

the copper-dish method, and 5 to 10 mg. per 100 cc. in the accelerated bomb test are considered the upper limits on gum for satisfactory fuel performance in storage and use, while 2 to 6½ hr. of induction period is considered the lower limit.

Significance of Acid Heat Tests.—The acid heat test using sulfuric acid as the reacting acid indicates roughly the total amount of olefins present in the fuel. It does not differentiate between the mono- and diolefins and this has caused some criticism when the method is used to indicate stability of the fuel in storage. It has been pointed out by certain writers[7,8] that the monoolefins do not form gum and that only certain of the diolefins, unless free of peroxides, do so. Therefore, within certain limits, a fuel of given acid heat will not always have the same stability characteristics as another fuel of the same acid heat. For rough determination of unsaturate content, however, the test is satisfactory.

The nitration acid heat test is similar to the sulfuric acid heat test in that it reacts the olefinic constituents, giving a temperature rise due to heat reaction. It is conceivable that it goes farther and reacts cycloolefins and possibly some of the aromatics. The proportion of nitric acid in the acid mixture is probably not sufficient for complete nitration of aromatics at room temperature.

Hubner *et al.*[9] quote opinions of several experts on the value of acid heat tests in connection with prediction of the stability of fuels, and these opinions are about equally divided in favor of and against. The difference was due to a disagreement on the ability of the accelerated gum tests alone to predict storage behavior. Therefore an accessory test such as one of the acid heat tests was deemed necessary by some to act as a control factor on unsaturated fuels in general.

Corrosion Properties.—Aviation gasoline should have no corrosive properties evidenced either by the fuel itself or in the products from its combustion. Sulfur and sulfur compounds are the principal source of corrosiveness in fuels, and specifications based on maximum sulfur content have been established. Also, corrosiveness is determined by means of a test wherein polished clean copper is exposed to the fuel. The fuel will not fulfill the specification if any gray or black corrosion is shown.

Sulfur compounds are undesirable in gasolines for other reasons than corrosive qualities. They reduce the lead susceptibility

of the gasoline and also act as catalysts for oxidation of certain types of hydrocarbons. With improved refining and conversion methods, sulfur contents of gasolines are being steadily reduced. It is probable that in the future sulfur-free fuels will be manufactured and the corrosion effects from this source will be entirely eliminated.

A high sulfur content is not desirable in a motor or aviation fuel because of the corrosive effects of the sulfur compounds as they exist in the fuel (such as mercaptans and sulfides) and because of the corrosiveness of the combustion products (sulfurous acid). It has been definitely proved that the degree of corrosiveness of the compounds as contained in the fuel and total sulfur content bear no relationship.[7] Some sulfur compounds are corrosive only if other types of compounds are present. To limit the potential corrosive effect of sulfur compounds, an average upper limit of 0.05 per cent total sulfur in aviation fuels has been established.

Two methods have been in use for the determination of corrosive properties of a motor fuel. These are the Copper-dish method and the Copper-strip method described in the Appendix.

Volatility and Vapor-pressure Properties.—Volatility (distillation range) and vapor-pressure properties are closely allied. The volatility specifications are determined by operating performance based on starting, fuel distribution, carburetor icing, and thermal efficiency (based on specific fuel consumption). A low 10 per cent evaporated point gives easy starting. Low 10 and 50 per cent points give better fuel distribution but tend to cause carburetor icing under given heating conditions. Low 10, 50, and 90 per cent points give lower efficiency in regard to specific fuel consumption. The ranges shown in Table 1–III for the various per cents evaporated have been generally standardized and accepted by fuel users and manufacturers. According to Hubner *et al.*[9] an increase in the 50 per cent point to 220 to 225°F. would make it easier for the refiners to meet the specifications. This has been done in certain cases on certain grades of fuel.

Vapor pressure specifications have been standardized at 7.0 lb. (Reid). This limit has been set as a result of practical experience based on observation of performance and vapor-locking tendencies. Vapor pressures above 7.0 lb. generally cause vapor lock.

Bridgeman *et al.*[5] correlated vapor-locking tendencies with vapor pressures of fuels and reported that the vapor-locking temperature decreases 2°F. for every 1,000-ft. increase in altitude. Based on the series of experiments a formula was developed giving the vapor-locking temperature for aviation gasolines at any altitude. This formula is given as follows:

$$T = 259 - 140 \log \frac{R \times 14.7}{}$$

where T = vapor-locking temperature.
  R = Reid vapor pressure, lb. per sq. in.
  P = atmospheric pressure, lb. per sq. in.

Using this formula, the vapor-locking temperatures for a 7.0-lb. Reid vapor pressure gasoline at various altitudes are as follows:

Feet	°F.
30,000	68 ✓
20,000	93
10,000	116

The vaporization property or volatility of an internal-combustion engine fuel is one of its most important characteristics. This is especially true of aviation fuel. A good aviation fuel for average aircraft engines should have the following properties in regard to vaporization: It should be sufficiently volatile to enable quick starting and ensure good fuel distribution to the cylinders under operating conditions. It should be low enough in volatility so that vapor lock will not occur and so that carburetor icing due to the cooling effect of the vaporization of the fuel will be prevented. It should also contain a maximum of heavier boiling material to give a higher combustion value per pound of fuel while still complying with the other volatility requirements. This latter requirement gives greater power per pound of fuel.

Two methods are used in practice to determine volatility and vaporization qualities of motor and aviation fuels. These are the A.S.T.M. Distillation method for determination of distillation range and the Reid Vapor Pressure method for determining vapor pressure.

Thermal Properties.—Thermal properties of aviation gasolines of interest to fuel users are the latent heat of vaporization and heat of combustion. Latent heat of vaporization is important

in that it affects mixture temperature and cylinder and piston temperature, all other things being equal. Higher latent heat materials lower these temperatures if the detonation characteristics of both are comparable. Thus, materials such as alcohols give lower operating temperatures than hydrocarbons. According to Heron and Beatty[3] isopropanol-water mixtures may be used effectively for short periods (as in take-off) if the proper procedure is used. This is feasible for only short periods of operation since the fuel consumption is greatly increased.

No specifications are established on latent heat of vaporization.

The heat of combustion of an aviation fuel is important because the higher the heat of combustion the greater is the range and load-carrying capacity due to lower fuel consumption. This is especially significant on cruising operation, and the use of hydrogen-deficient or oxygen-containing fuels is penalized accordingly. The hydrocarbons having the greatest heating value are the paraffin types, while the olefins give around 1.5 per cent less and the naphthenes around 3 per cent less heating value than the paraffins having the same number of carbon atoms. Aromatics have lower heats of combustion than the paraffins but the difference may be compensated for by their higher densities.

Specifications on heats of combustion range from 18,300 to 18,700 B.t.u. per lb.

Specific Gravity.—The specific gravity of an aviation fuel is of some importance in regard to the volume of the fuel compared to its combustion value. Since aviation fuels are somewhat limited as to hydrocarbon type, specific gravity is somewhat controlled indirectly by other specifications. A composition having a lighter specific gravity and a higher B.t.u. content per pound would be more advantageous than one of higher specific gravity, since the aircraft could attain more power or go farther per pound of fuel weight, all other things being equal. A heavier specific gravity fuel has an advantage over the other in that less volume is occupied by the fuel per unit weight.

Lead Susceptibility.—The problem of lead susceptibility of aviation fuels is of more interest to the refiner manufacturing the fuel than to the user, although the user is interested in corrosion effects and motor deposits caused by the use of tetraethyl lead. The user specifies the maximum amount of lead to be added to the fuel to be utilized in his engines and thus is

protecting himself to a certain degree. However, he has arrived at the specified limit as a compromise between quality and producibility of the fuel in the necessary quantity. Thus, it may be that a specification limit of 4 cc. per gal. is slightly higher than desired from a technical standpoint but is necessary to ensure a sufficient quantity being available.

The refiner on the other hand is interested in lead susceptibility since the greater the increase in antiknock value caused by the addition of lead the smaller the amount of expensive high-octane hydrocarbons that will be required in blending a gasoline of specified octane number. In most cases, the comparative cost of increasing octane rating by the use of lead is less than by the use of high-octane hydrocarbons. As an example, it would cost more to produce a 100-octane aviation fuel with a given straight-run gasoline base, isopentane, isooctane, and 2 cc. of tetraethyl lead than with the same components but using 3 cc. of tetraethyl lead.

Water Miscibility.—It is desirable to have an aviation fuel which is completely immiscible with water. Water dissolved in the fuel tends to separate at lower temperatures and will accumulate in suitable places in the fuel system and freeze. This is definitely to be avoided. Technically, the tendency of water to separate from the fuel in which it is dissolved is a function of its solubility-temperature curve rather than a function of the total amount held in solution. For example, an alcohol-water blend might contain a high percentage of water which would not settle at low temperatures. A gasoline-water solution, however, will separate. For specification purposes the tendency of a fuel of the gasoline type containing water to separate the water at lower temperatures is considered directly dependent upon the total amount of water dissolved. Specifications have been established ranging in tolerance of (gasoline for water) 0 to 2.5 per cent.

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HYDROCARBONS IN AVIATION FUEL AND IN AVIATION-FUEL MANUFACTURE

Aviation fuel derived from a petroleum source, whether natural or synthesized by one or a combination of several processes from petroleum materials, is composed almost wholly of hydrocarbons. In the past and at the present time, natural mixtures of hydrocarbons have comprised a greater proportion of the aviation fuels. The tendency is becoming more evident toward the inclusion of more and more pure hydrocarbons which are extracted or synthesized for that purpose and which have the correct properties desired. It has been recently predicted that the aviation fuel of the future will be composed entirely of pure hydrocarbons or known mixtures of them which have been produced by the blending of pure chemical compounds in the correct proportions to give the desired properties in the finished fuel.

Numerous studies by many investigators on the subject have shown that each type of hydrocarbon has definite properties in relation to its use as a motor fuel. Also, the different types have certain properties that affect their utilization in the various processes now in use for the manufacture of motor and aviation gasoline. Thus, before beginning the study of the complexities of aviation fuel manufacture, it is necessary to review the pertinent properties of the materials themselves that compose the fuel, the stocks to be synthesized, and the blending materials.
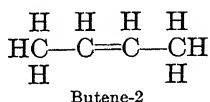
ALIPHATIC HYDROCARBONS

Aliphatic hydrocarbons are those carbon and hydrogen compounds which are classed as carbon-chain compounds in which there is no ring closure. Depending upon the degree of unsaturation they are further classed into paraffins, olefins, etc. The two types in which we are most interested are the paraffins illustrated

by butane as follows:

```
    H   H   H   H
    HC—C—C—CH
    H   H   H   H
        Butane
```
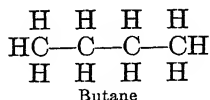
and the olefins illustrated by butene:

```
    H   H   H   H
    HC—C═C—CH
    H           H
        Butene-2
```

**Paraffins (Alkanes).**—The paraffins are represented by the general formula C_nH_{2n+2}, where n represents the number of carbon atoms in the chain. Thus, in the case of ethane, containing two carbon atoms, the empirical formula is C_2H_6 and the structural formula is

```
    H   H
    HC—CH
    H   H
     Ethane
```
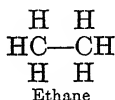
The paraffins are further classified into n-paraffins and iso-paraffins. The n-paraffins are single-chain hydrocarbons whose carbon atoms have no more than two carbon-to-carbon linkages and whose structural formulas are written with all the carbon atoms in a single row. Thus, n-butane, C_4H_{10}, is written as follows:

```
    H   H   H   H
    HC—C—C—CH
    H   H   H   H
        n-Butane
```
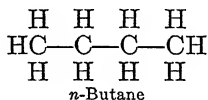
The isoparaffins have the same empirical formulas as the n-paraffins; but structurally they contain side chains, and the carbon atoms may have more than two carbon-to-carbon linkages. The properties of isocompounds may vary widely from those of the n-paraffins. An example of an isoparaffin is iso-butane, iso-C_4H_{10}, shown structurally as follows:

```
        H
        HCH
    H   |   H
    HC—C—CH
    H   H   H
       Isobutane
```
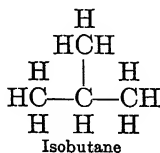
n-Paraffins (*n-Alkanes*).—The *n*-paraffins occur naturally in all petroleum oils to a greater or lesser extent. The paraffin base (Pennsylvania) crude oil contains the highest percentage of these materials while the Gulf Coast and California crude oils contain the least percentage. Natural gas is composed almost entirely of the lower molecular weight paraffin hydrocarbons.

In general, the normal paraffins are the most stable of the hydrocarbon family. They are very inactive chemically. At ordinary temperatures they are not acted upon by strong acids or

TABLE 1-IV.—*n*-PARAFFIN HYDROCARBONS

Hydrocarbon	Formula	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blend-ing-octane No.	Ani-line No.
Methane.........	CH_4	($-117.4°F.$) 0.1613	-257.9	8,000	110m 100+r		
Ethane..........	C_2H_6	($-127.3°F.$) 0.5462	-127.3	800	104m 100+r		
Propane.........	C_3H_8	($-43.6°F.$) 0.5824	-43.6	187	100m 100+r		
Butane..........	C_4H_{10}	0.5788	31.1	52.5	92m 95r	95r	1
Pentane.........	C_5H_{12}	0.6264	96.8	15.8	61r 58m	60r	1
Hexane..........	C_6H_{14}	0.6594	155.8	4.8	25r 34m	29r	-6
Heptane.........	C_7H_{16}	0.6838	209.1	1.4	0r, m	0r	-14
Octane..........	C_8H_{18}	0.7028	258.1	$1.0-$	-17m -28r	-19r	-21
Nonane.........	C_9H_{20}	0.7179	303.3	$1.0-$	-45r	-34r	-28
Decane..........	$C_{10}H_{22}$	0.7299	345.2	$1.0-$	-53r	-32r	-30

* For explanation of headings and symbols, see pp. 61–62.

alkalies. Table 1-IV lists the common normal paraffin hydrocarbons from the lightest, methane, to the 10-carbon chain, decane, and certain of their properties in which we are interested from the engine-fuel standpoint.

Examination of the data presented indicates that:

1. The density of the hydrocarbon, as well as the boiling point, increases with increase in number of carbon atoms.

2. The vapor pressure decreases with increase in number of carbon atoms. (In other words, the volatility of the compounds decreases.)

3. The antiknock values decrease with increase in number of carbon atoms.   These values are indicated by the octane rating, octane blending rating, and aniline number.

In general, the straight-chain compounds boiling within the present motor-fuel range consist of nothing lighter than 5 carbon atom compounds owing to the fact that those containing a lesser number are too volatile.   Nothing heavier than the 12 carbon atom compounds are included since their boiling points are too high.

Isoparaffins (Isoalkanes).—The isoparaffins are found to a small extent in natural gas and crude petroleum.   The isoparaffins from C_5 to C_9 are very valuable for use in, or as, high-antiknock fuels since they combine as a class high-octane rating, suitable boiling range, and reasonable volatility.   This type of hydrocarbon has in general the same properties as the *n*-paraffins. Under certain conditions, however, as will be seen later, they show the ability to combine with other hydrocarbons.   This important property is utilized in processes (discussed later) for the manufacture of aviation fuel.

Table 2-IV lists the physical characteristics of the important isoparaffins.

In general the vapor pressure of the compounds decreases with increase in number of carbon atoms in the straight chain, with approximately the same degree of branching.   The boiling points increase in the same manner.   Centralization of the molecule by moving the side chains closer to one another and toward the center of the molecule tends to decrease the vapor pressure and increase the boiling point.   The antiknock value increases with the number of side chains and with the centralization of the molecule for a given number of carbon atoms.   Also, the antiknock value tends to decrease with an increase in the number of carbon atoms in the straight chain.

Olefins.—The olefin hydrocarbons, also called *alkenes*, are represented by the general formula C_nH_{2n}, where n is the number of carbon atoms in the chain.   The empirical formula for ethene (or ethylene) is C_2H_4 and the structural formula

$$HC{=}CH$$
$$H \quad H$$
Ethene
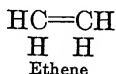
Olefins always have a double bond between two carbon atoms in the chain.

TABLE 2-IV.—ISOPARAFFIN HYDROCARBONS*

Hydro-carbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Oc-tane No.	Blend-ing octane No.	Aniline No.
Isobutane	C—C—C with C above center	0.5592	14	77.3	100+r		
2-Methyl butane (isopentane)	C—C—C—C with C above second	0.6200	82.4	21.0	90m	104m	9
2,2-Dimethyl propane (neopentane)	C—C—C with C above and below center	0.613	49.5	37.0	83m	116r	15
2-Methyl pentane (isohexane)	C—C—C—C—C with C above second	0.6562	140.4	6.5	73m	69r	4
3-Methyl pentane	C—C—C—C—C with C above third	0.6641	145.8	6.2	75m	84r	8
2,3-Dimethyl butane (diisopropyl)	C—C—C—C with C above second and third	0.6620	136.3	7.2	96r	106m	13
2,2-Dimethyl butane (neohexane)	C—C—C—C with C above and below second	0.6494	121.5	10.0	95m	97m	19
2-Methyl hexane	C—C—C—C—C—C with C above second	0.6787	193.5	2.0	45m	55r	0
3-Methyl hexane	C—C—C—C—C—C with C above third	0.6900	197.2	1.9	65r	65r	3
2,2-Dimethyl pentane	C—C—C—C—C with C above and below second	0.6736	194	2.0	93m	80r	8

TABLE 2-IV.—ISOPARAFFIN HYDROCARBONS.*—(Continued)

Hydro-carbon	Formula (C skeleton)	Sp. gr., D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
2,3-Dimethyl pentane	C—C—C—C—C with C on C2, C on C3	0.6944	193.5	2.0	85m	94r.	12
2,4-Dimethyl pentane	C—C—C—C—C with C on C2, C on C4	0.6729	177.4	3.0	82m	80r	8
3,3-Dimethyl pentane	C—C—C—C—C with two C on C3	0.6931	186.8	2.4	84m	98r	13
2,2,3-Trimethyl butane (triptane)	C—C—C—C with two C on C2, C on C3	0.6901	177.8	3.1	101m	116r	19
3-Ethyl pentane	C—C—C—C—C with C—C on C3	0.6986	199.9	1.7	60r	68r	4
2,3-Dimethyl hexane	C—C—C—C—C—C with C on C2, C on C3	0.7124	240.3	1.0−	79m	76m	
2,5-Dimethyl hexane (diisobutyl)	C—C—C—C—C—C with C on C2, C on C5	0.6949	228.7	1.0−	55m	69r	5
3,4-Dimethyl hexane	C—C—C—C—C—C with C on C3, C on C4	0.7195	241.7	1.0−	82m	80m	
2,2,4-Trimethyl pentane (isooctane)	C—C—C—C—C with two C on C2, C on C4	0.6919	201.6	1.5	100mr	100rm	16
2,2,3-Trimethyl pentane	C—C—C—C—C with two C on C2, C on C3	0.7162	230.4	1−	101m	105r	17

TABLE 2-IV.—ISOPARAFFIN HYDROCARBONS.*—(Continued)

Hydro-carbon	Formula (C skeleton)	Sp. gr., D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
2,2,3,3-Tetramethyl butane	C C | | C—C—C—C | | C C	0.7219†	223.6	1—	103m	130r	26
3-Methyl heptane	C | C—C—C—C—C—C—C	0.7057	246.4	1—	35m	......	−28
3-Methyl 3-ethyl pentane	C—C | C—C—C—C—C | C	0.7256	246.6	1—	91m	88m	
2,6-Dimethyl heptane	C C | | C—C—C—C—C—C	0.7049	273.2	1—	31m	36r	− 6
2,7-Dimethyl octane	C C | | C—C—C—C—C—C—C	0.7247	320.0	1—	34r	25r	−10
3,3,4,4-Tetramethyl hexane	C C | | C—C—C—C—C—C | | C C	0.770	321.8	...	123m	124r	29

* For explanation of headings and symbols, see pp. 61–62.
† Extrapolated—liquid.

The olefin group is classified into the *n*-olefin (*n*-alkene) and the isoolefin (isoalkene) class.

n-Olefins (n-Alkenes).—The *n*-olefin hydrocarbons are straight-chain hydrocarbons which have one or more double carbon linkages of the general formula C_nH_{2n} and the following structural linkage, —C≡C—. An example is butene-1.

$$
\begin{array}{cccc}
H & H & H & H \\
HC{=}C & -C & -CH \\
& H & H &
\end{array}
$$

Butene-1
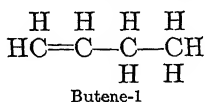
The *n*-olefins (alkenes) are found to a very small extent in natural gas, and the higher boiling members to a somewhat greater extent in certain crude petroleums. The principal occurrence of the lighter alkenes is in cracked products from the various cracking processes. In general, the dehydrogenation and molecule-splitting tendency under cracking conditions causes formation of unsaturated compounds.

This series of compounds is very reactive compared to the paraffin or alkane series owing to the double bond. Compounds having double-bond linkage between two or more carbon atoms react directly with the halogens such as chlorine and bromine, acids such as hydrochloric and sulfuric acid, and oxidizing agents. The tendency of the olefins to oxidize easily makes them unsatisfactory fuel materials wherein stability is absolutely necessary. Under certain conditions they react with themselves forming polymers, codimers, etc. Also, they will react with *n*- and isoparaffins (alkanes) under certain conditions of temperature and pressure, and in the presence of catalysts.

These properties are utilized in commercial processes for the production of hydrocarbon mixtures necessary for use in high-octane aviation and motor fuels.

Another unsaturated series, the acetylene or alkyne series, which should be mentioned, has relatively little importance in the consideration of high-octane fuels. This type of compound has the general formula of C_nH_{2n-2} and is represented by the substance acetylene, C_2H_2. The structural formula is

$$HC \equiv CH$$
Acetylene
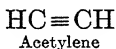
The triple carbon-to-carbon linkage makes this series highly reactive, much more so than the alkene or olefin series.

As in the case of the olefins, the acetylene series are found in products from cracking processes. There is very little if any occurrence of the alkyne series in crude oil and natural gas.

Table 3-IV gives the properties of the *n*-alkene series of hydrocarbons. (Some alkynes are included for the purpose of comparison.)

The boiling points and densities of this series increase with the number of carbon atoms in the chain and the vapor pressures decrease. The antiknock values decrease with an increase in

TABLE 3-IV.—*n*-OLEFINS (AND ALKYNES)*

Hydro-carbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Oc-tane No.	Blend-ing No.	Ani-line No.
Ethene....	C═C	(AtB.P.) 0.6104	−152.3	1,230	81m 100r	86r	
Acetylene..	C≡C	(AtB.P.) 0.6208	−118.5		80r		
Propene...	C—C═C	(AtB.P.) 0.6104	− 53.9	228	85m 100r	102r	
Butene-1...	C═C—C—C	(AtB.P.) 0.6255	− 22.1			112r	
Butene-2...	C—C═C—C	(AtB.P.) 0.6303	741.4 mm. 33.8	50	83m		
Pentene-1..	C═C—C—C—C	0.6429	86.2	19.0	92r	99r	
Pentene-2..	C—C═C—C—C	(30°C.) 0.6402	94.1	17.0		107m 125r	
Pentyne-2..	C—C≡C—C—C	(17.2°C.) 0.7127	131.9	8.0		108r	
Hexene-1...	C═C—C—C—C—C	0.6747	146.3	5.9	80r	85r	
Hexene-2...	C—C═C—C—C—C	(23.3°C.) 0.6792	150.8	5.5	78m 89r	100r	
Hexene-3...	C—C—C═C—C—C	0.6779	151.3	5.4	97r		
Heptene-1..	C═C—C—C—C—C—C	0.6976	199.6	1.8	54r	55r	
Heptene-2..	C—C═C—C—C—C—C	0.7034	208.4	1.4	70r	71r	
Heptene-3..	C—C—C═C—C—C—C	0.7015	201.2	1.7	84r	95r	
Heptyne-1.	C≡C—C—C—C—C—C	0.7322	211.3	1.2	84r	76r	
Heptyne-3.	C—C—C≡C—C—C—C	(19°C.) 0.765	222.8	1.0	40r	−30r	
Octene-1...	C═C—C—C—C—C—C—C	0.7159	252.5	1.0−	29r	25r	
Octene-2...	C—C═C—C—C—C—C—C	(30°C.) 0.7127	257.9	1.0−	57m		
Octene-3...	C—C—C═C—C—C—C—C	0.7181	253	1.0−		85m	
Octene-4...	C—C—C—C═C—C—C—C	0.7184	251.8	1.0−	74m	101m	
Octyne-2...	C—C≡C—C—C—C—C—C	(25°C.) 0.761	276.8	1.0−	66r	62r	
Nonene-1..	C═C—C—C—C—C—C—C—C	0.7308	294.8	1.0−	20r	15r	

* For explanation of headings and symbols, see pp. 61–62.

carbon atoms in the chain and also decrease when the double bond is shifted toward the center of the molecule (for a given number of carbon atoms).

Isoolefins (Isoalkenes).—The isoolefins are related to the *n*-olefins in the same manner as the isoparaffins are related to the *n*-paraffins. The addition of a side chain to a *n*-olefin makes it an isoolefin. For example, 2-methyl butene-2 is the *n*-olefin butene-2 to which has been added a methyl group on the 2 carbon,

TABLE 4-IV.—ISOOLEFINS*

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending, octane No.	Aniline No.
Isobutene	(C skeleton)	0.601	20.1	63	87m		
2-Methyl butene-2	(C skeleton)	0.6596	101.5	14.5	98r	157r	23
3-Methyl pentene-2	(C skeleton)	0.6948	153.5	5.1	79m	109r	14
2,3-Dimethyl pentene-2	(C skeleton)	0.7197	197.6	1.9		127r	21
2,4-Dimethyl pentene-2	(C skeleton)	0.6955	181.4	2.7	100+r	122r	20
2,2-Dimethyl pentene-4	(C skeleton)	(25°C.) 0.6883	161.2	4.1	. . . .	147r	27
2,2,3-Trimethyl butene-3	(C skeleton)	0.7029	172.4	3.3	89m	132r	23
3-Ethyl pentene-2	(C skeleton)	0.7217	203.4	1.6	96r	124r	20
2-Methyl hexene-5	(C skeleton)	0.6925	185	2.5	82r	83r	8
3-Methyl hexene-5	(C skeleton)	0.6969	189.1	2.2	85r	86r	9

TABLE 4-IV.—ISOOLEFINS.*—(Continued)

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
2,2,4-Trimethyl pentene-4		0.7164	214.7	1.2	86m	150r	32
2,2,4-Trimethyl pentene-3		0.722	220.1	1.0−	89m	144r	30

* For explanation of headings and symbols, see pp. 61–62.

thus

$$\begin{array}{c} \text{C} \\ | \\ \text{C—C=C—C} \end{array}$$
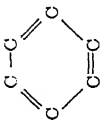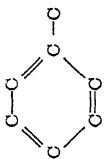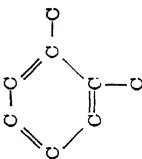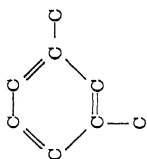2-Methyl butene-2
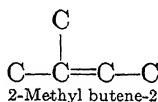
The isoolefins are found in products resulting from cracking processes and to a small extent in certain crude oils. They are rarely found in natural gas. The reactivity of the isoolefins is approximately the same as that of the normal olefins and is due to the presence of the double bond. They tend to polymerize and unite with other hydrocarbons, usually forming unsaturated or olefinic higher boiling compounds. Owing to the isomerized structure of the isoolefins, it is possible through catalytic polymerization to produce isocompounds of the required boiling range and isostructure to give high-antiknock-value fuel material when hydrogenated to saturate the double bond.

Table 4-IV lists some of the more common isoolefins and their properties.

The density and boiling point of the members of this series increase roughly with the number of carbon atoms in the chain. For the same number of carbon atoms in the base chain they also increase with an increase in the number and length of side chains. Most of the isoolefins boiling within the gasoline range have very

TABLE 5-IV.—AROMATIC HYDROCARBONS*

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
Benzene		0.8790	176.2	3.2	100+r	99r	10
Toluene		0.8660	231.4	1 –	100+r	124r	15
o-Xylene		0.8801	291.2	1 –	100+r	121r	17
m-Xylene		0.8641	278.6	1 –	100+r	144r	23
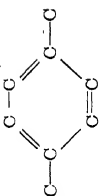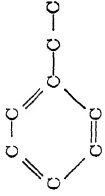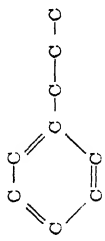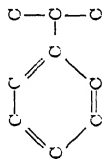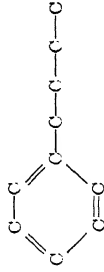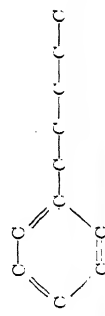
p-Xylene	26	146r	100+	1—	281.1	0.8610
Ethyl benzene	19	124r	98m	1—	277	0.8669
n-Propyl benzene	24	127r	99m	1—	319.1	0.8621
Isopropyl benzene (cumene)		124m	99.3m	1—	152.3	0.8633
n-Butyl benzene	20	115r	100+r	1—	361.6	0.8606
n-Amyl benzene	17	101r	......	1—	401.5	0.8582

TABLE 5-IV.—AROMATIC HYDROCARBONS.*—(Continued)

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb, abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
n-Hexyl benzene		0.8601	441.3	1 −			
n-Heptyl benzene		0.8570	455	1 −	....	46r	−3

* For explanation of headings and symbols, see pp. 61–62.

high octane numbers. The effect of structure of the molecule on octane number observed for the isoparaffins and the *n*-olefins is, in general, the same for the isoolefins.

AROMATIC HYDROCARBONS

The aromatic hydrocarbons are carbon-hydrogen compounds which are derivatives of benzene, a compound in which the carbon atoms are bonded together in the form of a ring and in which each carbon atom has one double linkage and one single linkage to adjacent carbon atoms. The empirical formula for this type of hydrocarbon is C_nH_{2n-6}. This is represented by benzene, C_6H_6, which has the following structural formula:

Benzene
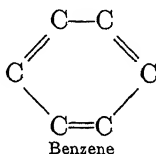
Aromatics having just one ring are called *mononuclear* aromatics. Two or more rings may be joined together to form *polynuclear* aromatics. Examples of this classification are naphthalene, a double-ring compound, and anthracene, a three-ring compound.

Aromatic rings may be joined to aliphatic compounds and through aliphatic chains to other compounds. In general, however, most of these types are not found in our normal aviation motor fuels and our consideration is limited to the mononuclear types with short side chains.

Aromatic compounds are found in all crude oils to some extent. Gulf Coast and California crude oils contain the highest percentage of this type of hydrocarbons. They are also formed in some catalytic conversion processes.

This series is chemically active and compounds of this type are acted upon by strong acids, the halogens, and oxygen. Upon oxidation, they form organic acids; upon extreme oxidation, the ring structure is destroyed. As a class, the aromatics have high-antiknock properties and high-antiknock blending ratings.
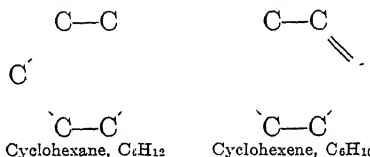
Table 5-IV lists some of the more common mononuclear aromatics with added side chains and some of their properties.

The boiling points and densities increase with the number of carbon atoms in the side chain.   The antiknock values decrease with an increase in the number of carbon atoms in the side chain.

NAPHTHENIC OR CYCLOPARAFFINIC HYDROCARBONS

Naphthenic or cycloparaffinic hydrocarbons are those which have the empirical formula C_nH_{2n} and which have the carbon skeleton arranged in the form of a ring.   The carbon atoms may be held together by single bonds, as in the case of the saturated cycloparaffins (cycloalkanes), or one or more double bonds may exist in the ring forming cycloolefins (cycloalkenes).

Examples of the two types are written structurally as follows

$$
\begin{array}{cc}
\mathrm{C-C} & \mathrm{C-C} \\
\mathrm{C} & \diagdown \\
\mathrm{C-C} & \mathrm{C-C} \\
\text{Cyclohexane, } C_6H_{12} & \text{Cyclohexene, } C_6H_{10}
\end{array}
$$

Cycloparaffins (Saturated Cyclics).—The saturated naphthenic type of compound is a cycloparaffin in which no double bonds exist in the ring.   Side chains and aromatic rings may be added to the nuclear ring.   These compounds are found to some extent in most crude oils and are mostly of complex structure.
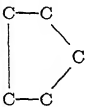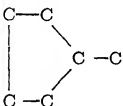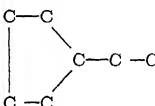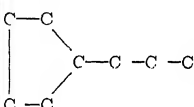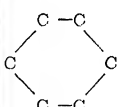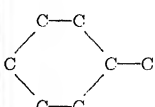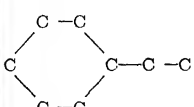
The naphthenes are relatively unreactive.   They are not very soluble in strong sulfuric acid and are fairly resistant to oxidation. Being saturated, reactions must take place in the form of substitution rather than addition.

Table 6-IV lists some of the saturated cycloparaffins with their properties. ·

The cycloparaffins (or cycloalkanes) increase in density and boiling point as the number of carbon atoms in the ring increases, and for the same nuclear ring an increase in the number of carbon atoms in the side chain increases the boiling point and density. The lighter cycloalkanes have higher antiknock values than the heavier, and for a given ring the addition of longer side chains lowers the antiknock value.
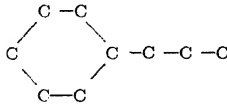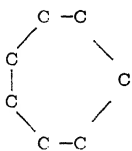
Cycloolefins (Cycloalkenes).—The cycloolefins are cyclic compounds having one or more double bonds in the ring.   As in the case of the cycloalkanes, there may be side chains or rings attached to the nuclear ring.   Compounds of the unsaturated

TABLE 6-IV.—CYCLOPARAFFINIC HYDROCARBONS*
(Saturated cyclic)

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
Cyclopentane	C—C, C, C—C (ring)	0.7460	121	13.0	100r 85m	141r	14
Methyl cyclopentane	C—C, C—C, C—C (ring)	0.7488	161.2	4.2	91r 80m	107r	4
Ethyl cyclopentane	C—C, C—C—C, C—C (ring)	0.7657	217.6	1.1	62r 55m	59r	1
n-Propyl cyclopentane	C—C, C—C—C—C, C—C (ring)	0.7765	267.4	1—	31r	16r	−10
Cyclohexane	C—C, C, C, C—C (ring)	0.7781	177.4	3.2	83r 77m	110r	7
Methyl cyclohexane	C—C, C, C—C, C—C (ring)	0.7692	214.2	1.2	75r 71m	104r	5
Ethyl cyclohexane	C—C, C, C—C—C, C—C (ring)	0.7878	268.9	1—	46r 41m	44r	− 3

* For explanation of headings and symbols, see pp. 61–62.

TABLE 6-IV.—CYCLOPARAFFINIC HYDROCARBONS.*—(Continued)

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Approx. vapor pressure, lb. abs. at 100°F.	Octane No.	Blending octane No.	Aniline No.
n-Propyl cyclohexane		0.7932	310.5	1—	18r	20r	—10
Cycloheptane		0.8100	243.0	1—	....	27r	— 6

* For explanation of headings and symbols, see pp. 61–62.

cyclic type have been found in most crude oils, particularly in the heavier fractions (gas oil-lubricant), and they usually have highly complex structures.

These materials are more reactive than the cycloalkanes owing to the presence of double bonds. Reactions may occur in the form of addition as well as substitution, and the compounds will react with sulfuric acid, halogens, and oxygen.
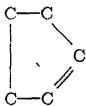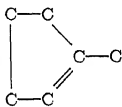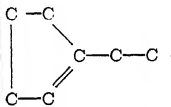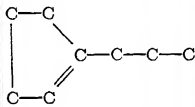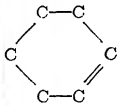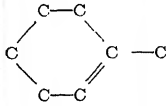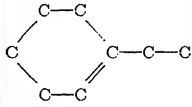
Table 7-IV lists a few of this type of compound and their properties.

The effect of structure on the properties of the cycloolefins is somewhat similar to the effect on the properties of the cycloalkanes. As a class, however, their antiknock values are greater than those of the cycloalkanes.

INFLUENCE OF HYDROCARBON TYPE ON FUEL CHARACTERISTICS

When we come to the study of the properties of the finished aviation fuel, we shall find that the specifications with which it must comply are very severe. Since the fuel is composed almost wholly of mixtures of hydrocarbons, those going into its make-up

TABLE 7-IV.—CYCLOOLEFINIC HYDROCARBONS*
(Unsaturated cyclic)

Hydrocarbon	Formula (C skeleton)	Sp. gr. D_4^{20}	B.P., °F.	Vapor pressure, lb.	Octane No.	Blending octane No.	Aniline No.
Cyclopentene		0.772	111.9	12	100+r	140r	16
1-Methyl cyclopentene		0.778	167.2	3.7	. . . . . .	143r	20
1-Ethyl cyclopentene		0.800	226.4	1—	. . . . . .	120r	12
1-n-Propyl cyclopentene		0.8062	269.6	1—	. . . . . .	96r	12
Cyclohexene		0.8098	181.4	2.6	84r	137r	10
1-Methyl cyclohexene		0.811	229.1	1—	83r	133r	20
1-Ethyl cyclohexene		0.8240	275.9	1—	. . . . . .	100r	13

* For explanation of headings and symbols, see below.

Explanation of Tables 1-IV-7-IV

Carbon skeleton. No attempt has been made to include more of the formulas than the carbon-atom relationship, showing the branches and the location of the double bonds.

Specific gravity. Unless otherwise indicated, the specific gravities of the compounds are those at 20°C. referred to water at 4°C. The values given in the tables were taken from Refs. 1 and 2.

Boiling point. The boiling points are those at 760-mm. pressure unless otherwise noted. The temperatures given are in Fahrenheit degrees converted from the centigrade data reported in Refs. 1 and 2.

Approximate vapor pressure. The vapor pressures listed are given in pounds per square inch absolute at a temperature of 100°F. These vapor pressures are not to be confused with Reid vapor pressures since they were estimated from true vapor pressure data. Owing to the method of determination, there is considerable deviation between true and Reid vapor pressures, the true being higher than the Reid.[5] These data are estimated from curves essentially designed for the vapor pressure relationships of the paraffin hydrocarbons. However, Beale[5] indicates that the slopes for the olefins and ring compounds are not widely different from those of the *n*-paraffins. These data therefore can be considered only as approximate and should not be used where accuracy is desired.[4,5]

Octane number and blending octane number. The octane and blending numbers are taken from several sources and the original references on individual determinations are not included. The octane numbers are followed by a small "r" or "m" indicating the test method used in their determination. The "r" indicates the Research method and the "m" designates the Motor method. Comparison of these methods is found in Table 8-IV.

must have properties that enable it to meet these specifications. Important characteristics of the fuel and its components are as follows:

1. Stability toward oxidation, gum, polymer, or tar formation.
2. Vaporization temperature or boiling point.
3. Vapor pressure at operating temperatures.
4. Antiknock value or resistance to preignition detonation.

On the basis of point 1 the paraffins, both straight- and branched-chain, are the least reactive and therefore are suitable in regard to chemical stability. The aromatic type are also relatively unreactive and are considered satisfactory. The naphthenes are more reactive and tend to form acids upon oxidation, but they may be utilized in aviation-fuel blends under certain conditions. These depend mainly on the type of ring, saturated or unsaturated, and the type of side chains and their degree of unsaturation. The olefins are relatively unstable and, as a whole, are classed as unsatisfactory for aviation-fuel blends because of this property.

On the basis of points 2 and 3, all the hydrocarbons listed, with the exception of some of the lighter compounds, are suitable.

Those boiling between approximately 100 and 300°F. and having true vapor pressures between 1 to 20 lb. per sq. in. make satisfactory components of an aviation fuel when blended properly.

From the standpoint of point 4 the straight-chain paraffins are the least satisfactory. The isoparaffins, olefins, aromatics, and naphthenes all have relatively high antiknock characteristics and in most cases high antiknock blending values. The blending octane values of the various types and individual compounds are of interest in that the blending octane value of one may be much higher than that of another yet the octane value of both pure compounds may be the same. Similar phenomena have been noted in the lead susceptibility (the rise in antiknock value for a given amount of tetraethyl lead added) of the various individual compounds and of mixtures of a predominant type.

CHEMICAL CONVERSION OF HYDROCARBONS

As the result of the Second World War the increased demand for military aviation fuel of 100 octane number has caused the development of many chemical conversion processes for hydrocarbons. These processes, which are discussed in detail later, convert hydrocarbons or mixtures of hydrocarbons, which are abundant but which are unsatisfactory aviation-fuel materials owing to their volatility, antiknock rating, etc., into pure compounds or mixtures of them that fulfill the necessary requirements. Thus through isomerization, dehydrogenation, and alkylation the abundant and cheap hydrocarbon, butane, is converted from a gas suitable mainly as a fuel gas into isooctane, which is an important component in aviation-fuel blending. Dehydrogenation, polymerization, and hydrogenation are also used extensively in the conversion of butane and isobutane to isooctane. Through isomerization alone the straight-chain paraffin, octane, with an octane value of −19 may be converted to one of the isooctanes having octane values from 27 to 103.

The study of these processes requires a knowledge of hydrocarbon chemistry. No longer does the refiner speak of motor fuel in such broad terms as gravity, distillation, end point, etc. Instead, he speaks of the composition of the blended fuel in terms of particular hydrocarbon compounds contained, their percentage and purity. Also, he must be familiar with the complicated hydrocarbon conversion processes that produce these

compounds and understand at least the fundamental chemistry of these conversions.

The type of motor fuel to be produced in the future depends largely on the design of the internal-combustion engines. It is possible that the motor of the future will be designed to burn a fuel consisting of a single pure hydrocarbon. Another possibility is that the fuel will be the same general type as that in use now but that the compression ratios in the cylinders will be increased greatly. In either eventuality, the petroleum industry will be required to enter into the manufacture of essentially pure hydrocarbons to meet these requirements. This, in addition to the production of pure hydrocarbons for the manufacture of synthetic rubber, will definitely establish the industry as the greatest chemical manufacturing industry from the standpoint of volume in all fields.

TABLE 8-IV.—COMPARISON OF OCTANE RATING METHODS*

	Motor method	Research method (1939)	C.F.R. Aviation method (1940) (I-C)
Speed..................	Constant, 900 ± 9 r.p.m.	Constant, 600 ± 6 r.p.m.	Constant, 1,200 ± 12 r.p.m.
Jacket temperature.......	Constant, ±1°F. Held between 209 and 215°F.	Constant, ±1°F. Held between 209 and 215°F.	Constant at 374 ± 2°F. w i t h i n ± 9°F.
Spark advance...........	Automatic, 26-0° at 5:1 compression ratio	Fixed, 13-0° for all compression ratios	Fixed, 35° for all compression ratios
Mixture temperature......	300°F. ± 2°F.	125°F. ± 2°F.	Intake air 125°F. ± 5°F. Mixture temperature 220°F. ± 2°F.
Intake valve.............	Shrouded	Shrouded	Plain
Fuel blends for checking engine.	49.1% c.p. benzene in A-6 equals 64.2% C-11 in A-6 (65 octane No.)	48.4% c.p. benzene in A-6 equals 72.5% C-11 in A-6 (70.0 octane No.)	85% S-1 in M-2 vs. c.p. benzene to give same thermal plug reading

* From table in "Octane Rating Relationships . . . ," Egloff and Van Arsdall, *J. Inst. Pet.*, **27** (210), 121 (1941).

The blending octane numbers have been either calculated or determined by actual test. The procedure used to determine part of the blending octane numbers was to dissolve 1 gram molecule of the hydrocarbon in a reference gasoline of 55 octane number and dilute the solution to 1 liter with the reference fuel. The octane number of the blend was then determined, and from the result, the blending octane value of the hydrocarbon was

calculated. The following formula[6] was used to calculate the blending octane numbers:

$$\text{Blending octane number} \quad \frac{O_B - O_R}{V} + O_R$$

where O_B = the determined octane number of the blend containing V fraction of the unknown.

O_R = the octane number of the reference fuel (determined by the same test method as O_B).

V = the fraction of hydrocarbon by volume.

Obviously, the blending octane numbers determined by different test methods and by using different proportions and reference fuels are not strictly comparable.[2,6,7]

Aniline number. Lovell, Campbell, and Boyd[8,9,10] reported some of the earliest complete data on antiknock values of the pure hydrocarbons. This work was based on the knocking characteristics of given amounts of hydrocarbon in solution in a reference gasoline compared to the knocking characteristics of aniline in the same reference fuel. The data were reported as aniline equivalent (or aniline number).

Quoting from a paper of Lovell, Campbell, and Boyd, "The relative knocking tendencies under these conditions have been evaluated in terms of aniline, a knock suppressor, and the unit of this evaluation has been called the aniline equivalent. A positive aniline equivalent indicates that the compound knocks less than the reference gasoline and represents the amount of aniline, expressed as the number of gram-mols $\times$ 100 per liter, which must be added to the reference fuel to produce a fuel that is equivalent in tendency to knock to a 1 molar solution of the compound in the reference gasoline—that is, to a solution containing 1 gram-mol of the compound made up to a volume of 1000 cc. with the reference gasoline. A negative aniline equivalent indicates that the compound knocks more than the reference gasoline and represents the amount of aniline, expressed again as gram-mols $\times$ 100 per liter, which must be added to the molar solution of the compound in the reference gasoline to make it equivalent in tendency to knock to the reference gasoline."

Since the same type of reference fuel and relatively the same conditions were used in determining aniline equivalent, many of the blending octane values have been calculated from these data.[6][8,9,10]

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CHAPTER V

THE PRODUCTION OF AVIATION-FUEL BASE STOCKS

There are many grades of aviation gasoline produced in normal times, and the differences among them are mostly those indicated by the octane rating and the stability specifications. Based on the octane rating there are grades ranging from 65 to 100 octane number. Under wartime conditions the attention of the refining industry is directed toward the production of enormous quantities of the higher grade fuels, 91 octane number, and the 100 octane number "fighting grade." It is generally accepted that the standard aviation fuel after the war will be the 100 octane grade, and some are of the opinion that the premium motor fuel will range from 90 to 100 octane number.

In present-day practice such high-antiknock-value fuels are composed of a blend of a special base gasoline having certain well-defined characteristics, one or more high-octane hydrocarbons, and tetraethyl lead. Owing to the characteristics of the base stocks, their production requires a special refining technique and only certain processing methods are suitable for their manufacture. Since these base gasolines represent an important component of high-octane aviation fuels, this chapter is devoted to their production and properties.

NECESSITY FOR A BASE STOCK

Base blending stocks, used in the manufacture of aviation fuels, are necessary for several reasons, both engineering and economical. From an engineering or utility standpoint a base stock provides the basis for the volatility or vaporization range, which is absolutely necessary in fuels to be utilized in aeronautical, internal-combustion motors of present-day design. Many pure hydrocarbons (and other substances), although they may have all the requisite properties but this important one, are not satisfactory because they have a very narrow boiling range. The base stock also provides a means of reducing the effect of certain undesirable properties of the other blending agents used in compounding the finished fuel. For example, certain com-

pounds (*e.g.*, olefins) have excellent blending properties in regard to octane number but, as a result of their chemical properties, have a deleterious effect on the fuel's performance. A suitable base stock will enable the use of such a compound in limited quantities, utilizing its advantages and diluting the effect of its harmful properties.

From an economic standpoint the use of a base enables the production of aviation gasoline at a lower cost than would be possible if the gasoline consisted entirely of materials made by relatively expensive, chemical conversion processes. From another economic angle, the use of a straight-run gasoline fraction as a base stock enables the refiner to utilize a relatively low-cost stock in a premium-priced fuel. This allows the major production cost for the finished aviation fuel to be allocated to the conversion methods producing the high-octane compounds.

PROPERTIES OF BASE STOCKS

The properties of the base stocks for aviation fuel are determined to a major extent by the specifications on the grade of fuel in question. With the exception of octane rating, the specifications for the important grades are essentially the same (see Chap. III). Therefore, with the exception noted above, the properties discussed here are the same for all bases used in the higher grades of aviation fuel.

The properties of an aviation gasoline base may be divided into two classes: those necessary and those desirable. Under the necessary qualities are the following:

1. *Stability.*—The base stock should be stable toward oxidation and not form gum in storage or in use.

2. *Low Sulfur Content.*—The base stock should have a very low sulfur content.

3. *Correct Distillation Range.*—The base should have a smooth distillation curve and boil within certain well-defined limits.

4. *Correct Vapor Pressure.*—The vapor pressure should be within certain limits depending upon the characteristics and proportion of other components to be blended with it. No butane should be contained in the stock.

5. *Low Freezing Point.*—The base stock should be of such a composition that it will not freeze or crystallize out any of its components, even at extremely low temperatures.

6. *Minimum Octane Rating.*—The base stock should have an octane rating of not lower than 65.   In special cases where stocks having high blending octane numbers are available the rating may be lower than this but in general it should be at least 65.

Although the characteristics listed above are those considered necessary, there are several others that are extremely desirable although not always available.   Some of these are as follows:

1. *High-octane Number (Unblended).*—As a general rule, the higher the unblended octane number of the base stock the less the quantity of high-octane compounds, such as isooctane and isoheptanes, that is necessary to raise the octane number of the finished blend to specification.   Thus, for a given production capacity of high-octane hydrocarbons, the total aviation fuel capacity of a refinery will be increased with an increase in octane number of the base stock.

2. *Good Lead Susceptibility.*—If the base stock has a good lead susceptibility, the amount of tetraethyl lead necessary in the finished fuel will be decreased.   Stating it another way, with the same amount of lead added, a decreased quantity of high-octane compounds will be necessary.

3. *Sulfur-free Stock.*—Owing to the reduction of lead susceptibility by even small amounts of sulfur, a sulfur-free stock would be desirable.

SOURCES OF AVIATION-FUEL BASE BLENDING STOCKS

Aviation-fuel base blending stocks may be procured from two general sources: (1) selected crude oils and natural gasolines and (2) conversion processes.   As we have noted previously, the stock consists of a low-boiling narrow-boiling range (100 to 300°F.) naphtha of low sulfur content, having an octane rating above 65.

Base Stocks from Crude Oils

According to Nelson[1] the octane ratings of gasolines produced from various crude types are somewhat as follows:

AVERAGE OCTANE NUMBER OF 398°F.-END-POINT GASOLINE

Paraffin base.. 40.2
Paraffin intermediate............................... 45.3
Intermediate or mixed........................... .... 56.0
Naphthene and naphthene intermediate.............. 64.9

These data indicate that the crude oil type most suitable for the production of aviation base blending stock is the naphthenic or naphthenic intermediate. It is also true that these crude oils are characteristically low in gasoline content and in many cases high in sulfur content. Nelson[1] listed over 160 naphthenic base crude oils as to the field from which they are produced, the gravity, the percentage of 400°F.-end-point gasoline contained, percentage of sulfur, and the octane number of the straight-run
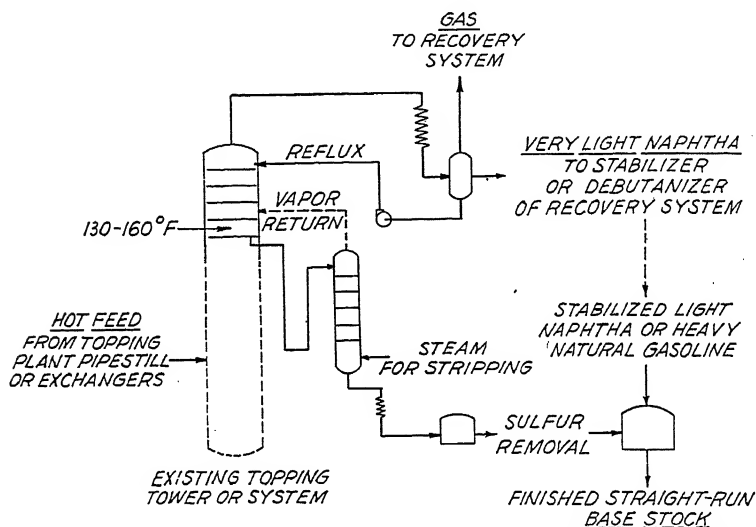
FIG. 1-V.—Process for making aviation-fuel base stock from crude oil distillation. (*Courtesy of Oil and Gas Journal.*)

gasoline. The octane numbers of the gasolines run approximately from 60 to 75. These ratings will be somewhat higher for fractions of 300°F. end point.

Other crude oils, although as a class not satisfactory sources for aviation-fuel base stock, may contain naphthas of suitable characteristics.

BASE STOCKS FROM NATURAL GASOLINES

Suitable aviation-fuel base stocks may be recovered from selected natural gasolines. Cody and Luntz[2] reported the manufacture of a 91 octane grade aviation fuel from a 26-lb. East Texas natural gasoline with no other blending materials except tetraethyl lead, and isopentane recovered from the natural

gasoline.   They conclude that the octane number of the depentanized gasoline should be at least 70 in order to produce a finished aviation fuel of 91 octane number without resorting to the inclusion of blending components obtained outside of the original natural gasoline stock (and tetraethyl lead).   It would be feasible, however, to use this type of base stock if alkylate or isooctane were available for blending.

METHODS OF PRODUCING BASE STOCKS FROM CRUDE SOURCES

The method of producing base blending stocks from crude oil and natural gasoline sources is usually one of fractionation and treating.
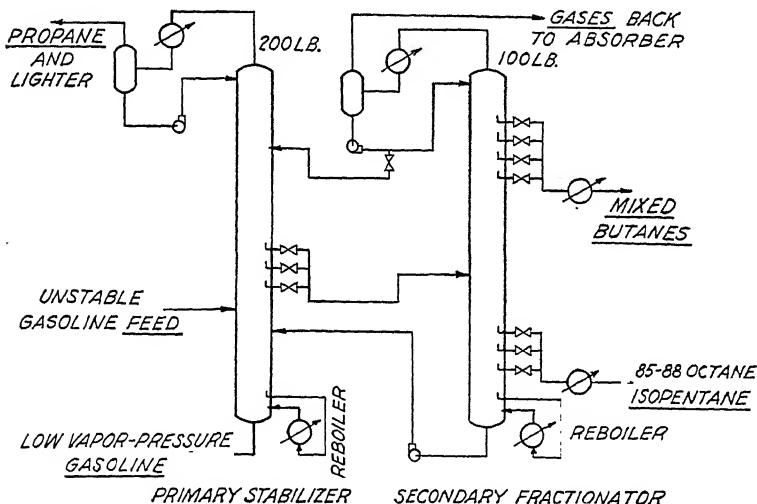
FIG. 2-V.—Process for making aviation-fuel base stock and isopentane from unstable naphtha or natural gasoline.   (*Courtesy of Oil and Gas Journal.*)

Typical flow diagrams are shown in Figs. 1-V and 2-V.   A method[3] of producing aviation-fuel base stock from crude oil is shown in Fig. 1-V.   This consists essentially of taking a narrow-boiling-range naphtha as an over-head or side-draw product from the crude oil topping tower.   Such a naphtha should have the following characteristics:

Initial, °F	120–140
90%, °F	235–250
E.P., °F	265–295
Vapor pressure, lb	2–4

If taken from a side draw and if a stripper is employed, no further treatment would be necessary except, perhaps, sulfur removal by sweetening, clay treating, or acid treating. If taken overhead, the naphtha would have to be debutanized to remove the high-vapor-pressure constituents.

In this method[3] the unstable naphtha or natural gasoline is fed to a stabilizer tower which yields light gases (propane, etc.) from the top, mixed butanes and pentanes as a side stream, and stabilized naphtha from the bottom. The butanes-pentanes are further fractionated in a second tower which yields gases overhead, a purified mixed-butane side stream, and, from a point below the feed inlet, an isopentane fraction. The heavier constituents from the bottom of the second tower are introduced into the primary tower at a point below the unstabilized gasoline or naphtha feed.

Aviation-fuel Base Stocks from Conversion Processes

Many conversion processes have been developed for the production of high-antiknock motor gasoline until, at the present time, the greater percentage of the regular and premium grades of this type of fuel consists of conversion products. These are the result of many and varied processes which grew from the necessity of the refiner to produce more gasoline per barrel of crude oil than is possible from straight distillation, and also the necessity for the production of motor fuel of higher antiknock value.

To fulfill this need the following general classes of processes have been developed:

A. Cracking:
    1. Thermal
        a. Liquid phase
        b. Vapor phase
        c. Combination
    2. Catalytic
        a. Liquid phase
        b. Vapor phase
B. Polymerization:
    1. Thermal
    2. Catalytic—nonselective
    3. Catalytic—selective

C. Combination type:
1. Aromatization
2. Gas reversion and polyforming
3. Isomerization
4. Reforming

With the exception of the processes listed under the combination type, there are many different modifications of each of the other types in commercial use. They all have advantages and disadvantages from the standpoint of motor-fuel production. Since the principal interest in this book is the relationship of such processes to the manufacture of aviation fuel, the following discussions will be based on that consideration.

Cracking

The term *cracking* may be defined as the destruction of a hydrocarbon molecule causing one or more breaks or scissions of the carbon-to-carbon linkage. Usually there are formed a paraffin and an olefin molecule from a larger paraffin. In commercial cracking practice, many reactions take place under cracking conditions. Based on the analyses of charge and products formed, the principal reactions are cracking, dehydrogenation, hydrogenation, polymerization, alkylation, and cyclization. The conditions of operation determine the type, number, and extent of the reactions taking place.

Cracking stocks may consist of any type of hydrocarbon stock from light gases to crude oils and heavy residual stocks. In most processes, however, naphthas, fuel oils, and gas oils are used. The cracking tendency of hydrocarbon types listed with decreasing tendency to crack is shown as follows:[4]

> Paraffins.
> Olefins.
> Diolefins.
> Naphthenes.
> Aromatics.

The cracking tendency for different sized molecules of the same hydrocarbon type increases with increase in size of the molecules.

Increased temperature increases the rate of cracking and the formation of unsaturated compounds. The effect of pressure is secondary in that it aids polymerization and effects gas reversion

through polymerization and alkylation. The effects of lengthening the time of cracking is to increase the amount of gasoline formed up to a maximum point. Beyond this limit, polymerization and condensation take place as well as dehydrogenation. This decreases the yield of gasoline and increases the formation of tars and cokes.

Thermal Cracking.—Thermal cracking yields a product containing large amounts of unsaturates, both mono- and diolefins and, where sulfur is present in the charge stocks, the sulfur content of the product is high. Thus, normally thermal-cracked naphthas are unsuitable for aviation-fuel base stocks. The olefin and sulfur content may be reduced by extensive treating methods but the loss in antiknock value, which is due primarily to the olefins present, is uneconomical under present conditions.

Catalytic Cracking.—Catalytic cracking produces a gasoline having, in general, a higher octane value and lower sulfur content than those produced by noncatalytic or straight thermal-cracking processes. Depending upon the operating conditions, the product may contain a much lower percentage of olefins. In such cases, the stability of the gasoline is much improved. The octane number of the product is partly due to the isomers and aromatics contained and therefore treatment for removal of the objectionable olefins will not result, in some cases, in a too severe reduction of antiknock rating. With sufficient treatment, therefore, certain catalytically cracked naphthas will form a satisfactory aviation-fuel blending base.

POLYMERIZATION

The term *polymerization* may be defined as the combination of smaller hydrocarbon molecules to form larger molecules without loss in carbon or hydrogen. This method utilizes the waste gases from cracking processes to form hydrocarbons boiling in the gasoline range. This increases gasoline yield and also quality since the polymer gasoline has a relatively high-octane number.

Only unsaturated compounds will combine under polymerization conditions, and the product or polymer is generally olefinic in nature.

Polymerization is carried out under elevated temperatures and pressures. High temperatures, in general, tend to crack rather than polymerize; low temperatures favor polymerization. High pressures favor polymerization. Catalysts are used under modified temperature and pressure conditions and give increased yields.

Thermal Polymerization.—Thermal polymerization effects combination of gaseous olefins under the influence of high temperature and pressure. Depending upon the process and the conditions of operation, various types of products are procured. The usual type, however, is highly olefinic and as a result is unstable. Treatment necessary to increase the stability would result in an uneconomical loss in octane number.

In one case[5] it is claimed that a thermal polymer gasoline can be produced with an octane number of 85 to 105 and containing 85 per cent aromatics. This type of polymer could be used satisfactorily as an aviation-fuel base provided that the olefins were removed.

Catalytic Polymerization.—The nonselective catalytic-polymerization processes yield highly olefinic products which are unsatisfactory because of their instability. Their high-octane ratings are for the most part due to the olefins contained, and reduction of the unsaturation by treating to improve stability would reduce the antiknock value too greatly. This is an economic factor that may change under certain conditions.

Catalytic selective polymerization, using as charge material the four carbon atom olefins, is one of the principal process sources of isooctanes. However, the octene polymer consisting of monoolefins (isooctenes) must be hydrogenated to form the corresponding octanes before use. This makes the polymer stable. (Complete discussion of this process is found in Chap. VI.)

Combination-type Processes.—The class of processes that makes use of several different types of reactions simultaneously is called *combination-type processes.* Many authors prefer to class all high-temperature, high-pressure conversion methods under the general classification of cracking. However, here it is preferred to discuss those which are unique in some phase of their operation such as feed type, catalyst used, or type of product, separately. The processes that are of commercial importance in the production of aviation-fuel base stocks are described on the following pages.

Aromatization

The term *aromatization* is applied to the formation of aromatic compounds from aliphatic or straight-chain hydrocarbons. This involves the formation of rings and the simultaneous or subsequent dehydrogenation to aromatic structures. Because of this mechanism, Grosse *et al.*[6] have termed the reaction *dehydrocyclization*.

Originally, it was believed that aromatization (applied to the formation of benzene from aliphatics) could be attained only through the polymerization of a compound such as acetylene. Benzene, C_6H_6, was produced successfully by the polymerization of acetylene C_2H_2 (3 molecules forming 1 molecule of C_6H_6). More recently, it has been found possible to form aromatics both catalytically[6,7,10] and thermally[5,8,9] from aliphatics, or straight- and branched-chain hydrocarbons. As a result, *n*-heptane may be converted to toluene by the steps shown below.
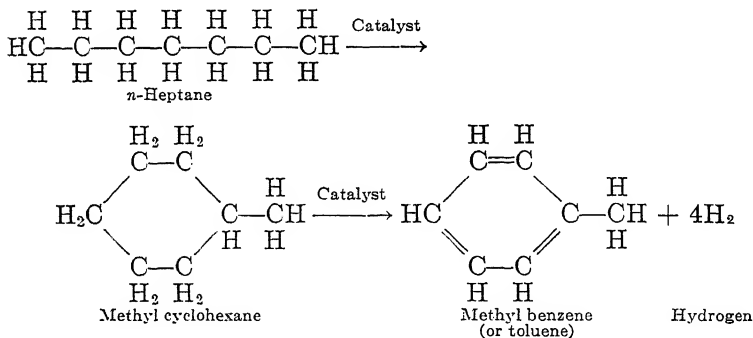
Similarly, *n*-hexane and the *n*-hexenes may be converted to benzene, *n*-octene and *n*-octenes into *o*-, *m*-, *p*-xylenes and ethyl benzene, etc.

Experimental work reported in the literature indicates that the emphasis has been placed on the use of catalytic agents to effect aromatization. Catalysts that have been found effective are the oxides of metals of the IVth, Vth, and VIth groups of the periodic system. The oxides investigated were generally supported on carriers of low catalytic activity such as alumina and magnesia, and the amounts were relatively small in proportion to the amounts of reactants, *i.e.*, small molecular proportions.

Some of the catalysts that were investigated are listed as follows:

Cr_2O_3............................... Not supported on inactive base
Mo_2O_3............................... Not supported on inactive base
Cr_2O_3............................... Supported on inactive base
A mixture of V and Cr oxides............ Supported on inactive base
A mixture of V and Mo oxides........... Supported on inactive base
A mixture of Cr and Mo oxides.......... Supported on inactive base
A mixture of V, Cr, and Mo oxides....... Supported on inactive base

According to Grosse *et al.*,[6] the preparation of the catalyst to secure the right "surface availability" is important to the conversion efficiency. Surface availability is defined as the surface area in square centimeters per gram of catalyst, accessible to the gases or vapors. Also of importance are the factors of surface condition of the active metal oxide catalyst, the surface condition of the catalyst (oxide plus supporting medium), and the physical and chemical relationship between the oxide catalyst and the carrier.

The catalysts used in the unsupported condition produced partial cyclization at temperatures of 842 to 932°F. At higher temperatures they tended to crystallize and lose their activity. With the same catalysts supported on carriers, they were found to be effective at higher temperatures and had relatively longer life (1,000 hr.).

In one experiment described, pure *n*-heptane was aromatized at 932°F. over chromic oxide-on-alumina catalyst for 1 hr. at atmospheric pressure. The liquid space velocity was 3.6 volumes per volume of catalyst per hour. In the liquid product (yield—98.1 weight per cent of charge), 12.1 per cent of toluene, 11.5 per cent heptenes, and 75.5 per cent of unreacted heptane were found.

There are a number of patents on catalytic aromatization. Two established commercial processes, *Hydroforming* and *Cycloversion*, are in operation. There are several operating units utilizing these processes and more are in the process of construction. These are discussed later in this chapter.

Thermal aromatization has been investigated also and there is one process, called the *Forward process*[9] which is said to have commercial possibilities. Another process, which may be operated to yield a product containing a high percentage of aromatics,

is the Polyform or Gas Reversion process.* In one case[10] thermal polyforming produced a distillate containing 11 per cent and 13 per cent, respectively, of toluol and xylol.

In addition to the processes which were designed for the production of gasolines containing relatively large amounts of aromatics and those which can be made to produce aromatic gasolines by changing the conditions of operation, much of the thermal-cracking capacity can be utilized for aromatization purposes. Cooke[10a] claims that if the pressures of thermal-cracking units are lowered to around 15 lb. per sq. in., if temperatures are raised to 1200 to 1400°F., and if provision is made for increased time of exposure of the vapors to these temperatures, aromatization is effected and, in addition, large quantities of butenes and butadienes are produced. Such operation requires the use of a clean, vaporizable charging stock and requires provision on the unit for a quick quench to prevent excessive coking. The aromatic fractions may be separated by distillation and solvent extraction.

By means of aromatization it is possible to produce fuels of high-antiknock value, with reasonable stability, and boiling within the correct boiling range. Such fuels can be used for aviation fuels and aviation-fuel bases.

Three processes, two involving catalytic aromatization—Hydroforming and Cycloversion—and one involving thermal aromatization—the Forward process—are described in the following pages.

Catalytic Aromatization—The Hydroforming Process.[11]—In the Hydroforming process which is in commercial operation in several plants at the present time, low-octane gasolines are converted into high-octane fuels, catalytically, in the presence of hydrogen. Normal paraffin hydrocarbons of six or more carbon atoms are cyclicized and dehydrogenated partly to aromatic hydrocarbons. There are only small amounts of olefins formed (presumably owing to the presence of hydrogen), and the gasoline product is relatively stable.

The Hydroforming process was developed by the research organizations of several companies, including primarily the M. W. Kellogg Co., the Standard Oil Development Co., and the Standard Oil Co. of Indiana. The process is licensed by the

* For a description of this process see p. 85, Chap. V.

Standard Catalytic Co., which has important patent rights for this and related processes.

CHEMISTRY OF PROCESS.—For typical reactions, see those on page 76. The presence of hydrogen prevents the excessive dehydrogenation of the hydrocarbons and thus inhibits excessive olefin formation.

FLOW.—The accompanying flow diagram Fig. 3-V illustrates the flow and arrangement of equipment in the hydroforming plant of the Pan American Refining Co. at Texas City, Tex. The principal equipment consists of the heating furnace equipped with coils for heating the charge naphtha and recycle gas sep-
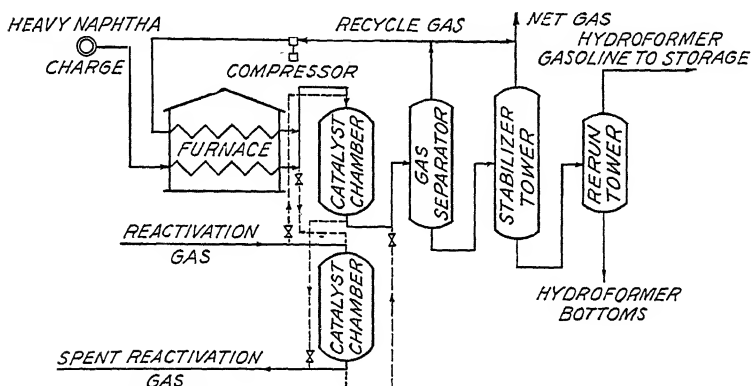
FIG. 3-V.—Flow diagram of the Hydroforming process.   (*Courtesy of Oil and Gas Journal.*)

arately, catalyst chambers, gas separator, stabilizer, and rerun towers.

The flow is as follows: The feed, consisting of heavy naphtha, is heated in a preheater furnace.   In the same furnace, but different coils, the hydrogen-rich recycle gas is heated simultaneously. The two streams are mixed thoroughly upon leaving the furnace, and the mixture is conducted to the catalyst chamber which is maintained under considerable pressure.   The reaction products are cooled to atmospheric temperature and sent to a gas separator. Part of the gas separated is recycled back into the system and part is sent into the fuel system.   The liquid hydrocarbon mixture from the separator is taken to a stabilizer tower in which all the remaining gas is removed.   The stabilized gasoline is

then rerun in a fractionating tower and the heavier constituents (heavy polymers) are separated.

ELEMENTS OF OPERATION. *Feed.*—The feed to this process consists of low-octane heavy naphtha derived from cracking plant operation. It may consist of a blend of cracked and straight-run naphtha or straight-run naphtha alone. The hydrogen-containing gas is obtained from the Hydroforming process itself, and the quantity produced is more than sufficient for the needs of the process.

Catalyst.—The catalyst in use in this process has not been announced but probably consists of a metallic oxide of the type described in the previous section adsorbed on an inert carrier. It is in granular form and arranged in chambers in such a manner that a high surface availability is offered to the hydrogen-hydrocarbon mixture. The life cycle of the catalyst is limited, owing to gradually increasing amounts of coke deposited on its surface during the operation. As this deposit increases, the efficiency of the catalytic agent decreases and this necessitates periodic reactivation. This is done by taking the catalyst tower, which has lost its efficiency, out of operation and burning off the coke deposit by circulating through it flue gases containing small amounts of air. The rate of burning is controlled by the amount of air admitted. Elevated pressures and carefully controlled temperatures are maintained throughout the reactivation period.

Temperature and Pressure.—The temperature at which this process operates is said to be around 100°F. and the pressure is considerably higher than atmospheric.

YIELDS AND QUALITY OF PRODUCT.—Owing to the flexibility of the Hydroforming process, it is possible to produce gasolines of a wide range of antiknock values up to 90 A.S.T.M. octane number. It is possible to operate the process on a 40- to 45-octane-number feed naphtha to produce an 80 per cent yield of gasoline of 80 A.S.T.M. octane number. Of this gasoline, 40 to 50 per cent is aromatic, and of the aromatic content, 15 to 20 per cent is toluene and the rest xylenes and higher aromatics.

The characteristics of a typical feed stock and gasoline are given in Table 1-V.

By operating the Hydroforming process under certain conditions (not specified), it is claimed that a product can be made

TABLE 1-V.—CHARACTERISTICS OF FEED AND PRODUCT

	Charge	Product
Gravity A.P.I.	51.4	51.3
Octane No. A.S.T.M.	47.2	77.0
Reid vapor pressure, lb	0.4	8.2
Distillation:		
Initial, °F	222	99
10%, °F	250	174
50%, °F	292	270
90%, °F	367	339
Max., °F	436	368

having up to 80 per cent aromatic content. Under other conditions it is possible to make a high-grade aviation gasoline.[11]

COMMERCIAL APPLICATION.—This first commercial hydroforming plant was started in Texas City in 1941. The toluene production capacity of this unit, representing around 5 million gallons, was at that time approximately 25 per cent of the total toluene production of this country in 1939.[11] There are several such units in operation and building at present.

Although toluene production is the important application of this process under present conditions, it is also an important source of aromatic-type aviation gasoline.

Catalytic Aromatization—The Cycloversion Process.[11a,11b]—A new catalytic aromatization process called the *Cycloversion process* was announced in the early part of 1943 by the Phillips Petroleum Co. This conversion method is capable of reforming naphthas from thermal cracking into highly aromatic type gasolines suitable as aviation gasolines. The charge stocks may consist of fractions ranging from light gasolines to heavy gas oils, but for aviation gasoline manufacture the best stock appears to be selected naphthas from thermal cracking or gas reversion operations.

The flow in the cycloversion process is as follows: The feed naphtha is passed through a heater where it is vaporized and brought to the required temperature. During this period, thermal decomposition takes place. The partly decomposed feed vapors are then passed through the catalyst chambers at moderate pressures and relatively high flow rates, and the aromatization is effected.

The continuous operation is achieved by alternate operation and revivification of two or more catalyst cases.   Reactivation of the catalyst is carried out by the controlled burning of the carbonaceous deposit on the catalyst.   Process periods for the production of aviation stocks range from 1 to 5 hr.   The catalysts are rugged and resist poisoning and are capable of withstanding high temperatures without injury.   Steam may be used in both the reaction cycle and reactivation cycle without harmful effects.

At least one plant using this process was in operation by the first part of 1943.

Thermal Aromatization—The Forward Process.[9]—Although several thermal processes have been found to produce a product
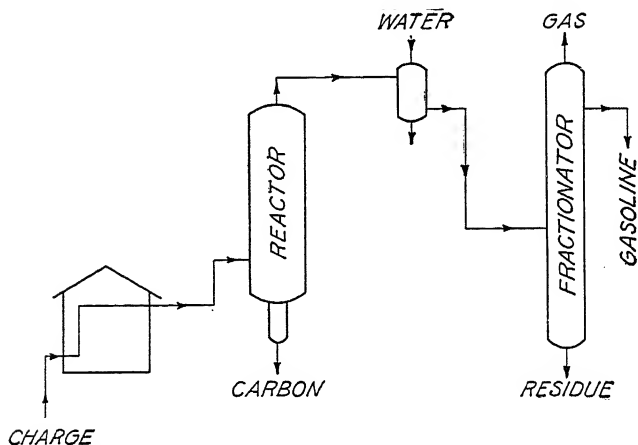
FIG. 4-V.—Schematic flow diagram of the Forward process.

containing relatively large amounts of aromatics, few have been specifically developed for the conversion of chain compounds existing in crude oil to aromatics.   One of these is the Forward process.   In this method thermal cracking of a gas oil distillate is resorted to and a synthetic crude oil is produced.   The gasoline fraction from the crude oil contains a high percentage (70 to 75 per cent) of substituted aromatic compounds.   The gasoline product is suitable, when fractionated to the correct boiling range, for use as aviation fuel or an aviation-fuel base, since it is of high-antiknock value, has the required stability, boils within the correct boiling range, and has a very low freezing point.   The latter characteristic is decidedly advantageous over that of

benzol fuels in that they have relatively high freezing points owing to the high freezing point of benzene.

The Forward process was developed by the Doherty Research Co., formerly connected with the Cities Service Oil Co.

CHEMISTRY OF PROCESS.—The chemistry involved in this process is not clearly defined. Apparently, the following reactions take place: cracking and dehydrogenation of the larger hydrocarbon molecules contained in the gas oil to paraffins, olefins, and probably hydrogen; cyclization of the paraffins and olefins; and probably alkylation of the aromatics formed by the smaller molecules of paraffin hydrocarbons.

FLOW.—The plant described in the literature is a semicommercial or large pilot plant and no flow diagram is given. From the description offered, however, Fig. 4-V was derived as a general flow diagram. The equipment consists essentially of a heating furnace containing a long heating coil, a reaction chamber, a condenser, and fractionating equipment.

In this unit the charge oil (a gas-oil distillate) was preheated to above 900°F. and passed through a 1-in. cracking coil 2,300 ft. long at the rate of 180 gal. per hr. The temperature at the coil exit was about 1050°F. From the cracking coil the products passed to a carbon settling chamber maintained at around 1050°F. and a pressure of around 225 lb. per sq. in. The cracked vapors, passing off from the top of the chamber, were chilled by means of a water spray and passed to a condenser. The uncondensible gas, containing probably some gasoline constituents, was not recovered in the units described. The vapors, condensed at 30 lb. pressure, constituted a synthetic crude oil which was fractionated in suitable equipment to recover the gasoline fraction.

ELEMENTS OF OPERATION. *Feed.*—The charge consisted of a distillate gas oil. Gas oils from almost any crude source serve as satisfactory charging stocks provided selected operating conditions are used.

Temperature and Pressure.—The temperatures of operation were as follows: preheat, above 900°F.; coil exit, 1050°F.; settling chamber, 1050 to 1075°F. The pressure in the settling chamber was maintained at 225 lb. per sq. in. and 30-lb. pressure was maintained in the condenser.

Time of Contact.—The contact time, or heating time, is exceptionally long in this type of process, ranging from 20 to 30 min

in the coil and reaction chamber.   This is reasonable since it is
known that long reaction times under cracking conditions favor
aromatic-ring formation.

YIELDS AND QUALITY OF PRODUCT.—Operation of this unit
under the conditions described above yielded the following
products from the synthetic crude produced:

	Per Cent
Gasoline (410°F., E.P.)	51.6
Benzene bottoms	5.8
Residuum (1.2 sp. gr.)	41.7
Loss	0.9

The gasoline fraction had the properties listed in Table 2-V.

TABLE 2-V.—CHARACTERISTICS OF GASOLINE FRACTION
FROM THE FORWARD PROCESS

Aniline point, °C	0.0
Distillation:	
Initial, °F	133
10%, °F	217
20%, °F	230
50%, °F	266
80%, °F	317
90%, °F	343
E.P. °F	399
Gravity, A.P.I.	31.3
Gravity, specific	0.869
Molecular weight	105
Refractive index	1.4926

Hydrocarbon analyses by two methods indicate the composi-
tion of the gasoline to be that as listed in Table 3-V.

TABLE 3-V.—HYDROCARBON ANALYSES OF FORWARD PROCESS GASOLINE[9]

	Method 1	Method 2
Olefins	4.8	8.6
Aromatics	85.4	91.4
Naphthenes	9.8	0.0
Paraffins	0.0	0.0

Qualitative tests on the gasoline fraction indicated the follow-
ing compounds: benzene, toluene, xylenes, isopropyl benzene,
n-propyl benzene, o-methyl ethyl benzene, methyl isopropyl
benzene, p-methyl ethyl benzene, mesitylene, pseudocumene,

sec-butyl benzene, isobutyl benzene, o- and p-methyl isopropyl benzene, n-butyl benzene, o-methyl propyl benzene, o- and p-diethyl benzene, isoamyl benzene, n-amyl benzene, and naphthalene. The compounds above mesitylene in molecular weight boil higher than 325°F. and in general are unsuitable for regular aviation fuel because of this. However, many of them would be satisfactory for aviation safety fuel.

COMMERCIAL APPLICATION.—The Forward process has not been used in commercial installations as far as is known. However, since the demand for increased quantities of aromatics has become great under war conditions, it is possible that this process may be adopted for commercial production of aromatic compounds and aromatic-type aviation fuels.

The Gas Reversion or Polyform Process[8,10,12,13]

The Polyform process produces a gasoline of suitable characteristics which may be used as a base blending material for aviation gasoline. In operation the process differs from conventional thermal-cracking practice in that it processes the cracking stock in the presence of varying amounts of the normally gaseous hydrocarbons, particularly propanes and butanes. It is operated at higher temperatures and pressures and at higher conversions per pass, without the excessive coking of the tubes that would be encountered in normal thermal practice.

By adjusting the operating conditions and by suitable treatment of the product, it is possible to produce, simultaneously, both an aviation gasoline base of 77 to 79 octane number and an aviation safety fuel of 80 octane number.

The Polyform process is covered by patents of the Gulf Oil Corp. and the Phillips Petroleum Co. and is licensed under the Lummus Co.

CHEMISTRY OF PROCESS.—The chemistry of gas reversion is very complicated. Many reactions occur and the reaction mechanisms vary. According to Bogk et al.,[12] it is believed that in this process a substantial portion of the liquid petroleum fraction (naphtha) is converted through the mechanism of thermal cracking into gaseous olefins and paraffins. These olefins are polymerized into higher olefins in the gasoline boiling range and some are combined with the paraffins in alkylation reactions. Similarly, the gaseous paraffins (C_3 and C_4) introduced

into the system, are first partly or wholly cracked or dehydrogenated to lower olefins, and the resulting olefins and residual paraffins are immediately polymerized or alkylated into higher boiling materials. In general, the mechanism of polymerization predominates, with alkylation taking place to a lesser degree.

Under certain conditions, dominated by the time of contact in the cracking zone, larger quantities of hydrocarbons boiling in the gasoline range are formed, the gasoline fraction becomes richer in aromatics, and tar and eventually carbon formation begins. This indicates dehydrogenation combined with aromatization.
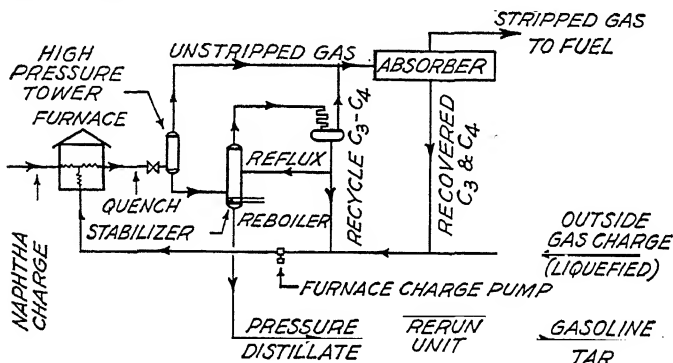
Fig. 5-V.—Schematic flow diagram of the Naphtha-gas Reversion process. (*Courtesy of the A. P. I.*)

Flow.—There are two distinct types of flow in use in this process. They are designated as (1) gas reversion or naphtha-gas reversion and (2) polyforming or naphtha polyforming. Essentially, the processes are similar, with the difference existing primarily in the method of introducing the gas, both recycle and virgin, into the system. Also, there are slight differences in operating conditions of temperature, pressure, and time of contact.

The schematic diagram shown in Fig. 5-V is that for the naphtha-gas reversion system. The flow is as follows: The recycle gas and external gas charges are liquefied, combined, and conducted to a heating coil in the furnace. At an optimum point in the coil, the preheated naphtha charge is injected into the gaseous stream and the total mixture passes through the remainder of the coil. The products from the furnace are cooled, and

temperature control is maintained by means of quench oil. This usually is a gas oil introduced into the transfer line. The product mixture is then fractionated in a high-pressure tower to separate the noncondensible gases from the remainder of the product. The gases are passed through an absorber to remove all of the recoverable C_3 and C_4 gases for recycle. The bottoms from the high-pressure tower are stabilized in a second tower with the C_3 and C_4 gases removed overhead and recycled. The bottoms (pressure distillate) are rerun to separate the gasoline fraction from the gas-oil and fuel-oil fractions. The gasoline fraction is then treated and finished.
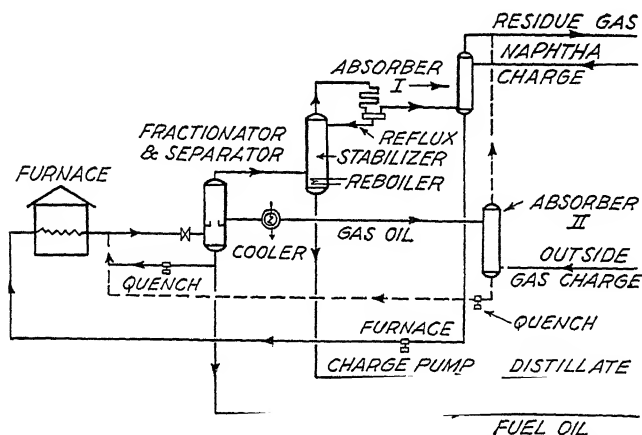
Fig. 6-V.—Schematic flow diagram of the Naphtha-Polyform process. (*Courtesy of the A. P. I.*)

The schematic flow diagram shown in Fig. 6-V is that for the naphtha Polyform process. In this process the naphtha feed is used as an absorbent for the recycle C_3 and C_4 gases coming from the top of the stabilizer tower. Thus, the charge naphtha enters the system through an absorber where it becomes enriched with the recycle C_3 and C_4 gases. This enriched mixture is preheated and passed through the furnace. If gases from an outside source are to be utilized, they are absorbed in a second absorber with the gas oil from the fractionator as an absorbent. This enriched gas oil is introduced into the transfer line from the furnace to the fractionator, as quench oil. The quenched product from the furnace, containing uncondensible gases, C_3 and C_4 (unreacted and from the enriched quench oil), the gasoline

product, and heavier fractions, passes to the fractionator wherein the gases, C_3 and C_4 hydrocarbons, and gasoline are taken overhead, fuel oil from the bottom, and gas oil, for absorbing fresh outside C_3 and C_4 feed, from the side. The gasoline and gas pass to a stabilizer wherein the gases are taken overhead to the naphtha absorber, where the C_3 and C_4 are absorbed for the charge. The uncondensible gases leave the system. The bottoms from the stabilizer are taken to rerun and treating units.

ELEMENTS OF OPERATION. *Feed.*—The character of the feed naphtha naturally varies with the type of crude oil from which it is derived. The distillation range of the charge naphtha is approximately 200 to 450°F. Almost all types of crude oils will produce naphthas satisfactory for this process. (Although, in this discussion, we are concerned with naphtha polyforming and naphtha gas reversion, it must be added that this process is capable of taking as a charge stock, gasoline, naphtha, and gas oil, provided suitable adjustments are made in operating conditions.)

The gas charge to gas reversion and polyforming essentially consists of C_3 and C_4 hydrocarbons. These consist of propene, propane, butenes, isobutene, butane, and isobutane in proportions depending upon the source, *i.e.*, whether or not it comes from cracking, natural gasoline stabilization, or gas recovery system.

The ratio of gaseous feed to naphtha feed is somewhat critical. There is an absolute minimum limit of the dilution of the heavier oil with the liquid gas fraction and also an absolute maximum limit. In a once-through reconstruction of a straight-run naphtha, short of coking, the recycle ratio of propane to the amount originally charged should range from 7 to 10. Butane recycle ratios range from 3 to 5. The ratio of total liquid-gas feed to the naphtha charge is usually approximately 1 to 1 to 2 to 1.

Table 4-V lists representative naphtha and gas feeds used in commercial installations.

Temperature and Pressure.—The temperature and pressure at which the process operates depend upon several variables such as the composition of the feed and ratio of liquid gas to naphtha, the recycle ratio of gaseous constituents, the reaction time, the type of product desired, and the yield. These are dependent variables,

and a change in one effectively constitutes changes in the others. Higher pressures tend to increase polymerization of olefins, particularly when they are diluted with paraffins, and also tend to increase alkylation reactions. Higher temperatures tend to increase the reaction rates, to increase the formation of cyclics, and to dehydrogenate them to aromatics. At a critical point,

TABLE 4-V.—TYPICAL FEEDS FOR NAPHTHA POLYFORM AND NAPHTHA GAS REVERSION UNITS

	Gas reversion		Polyform	
	1	2	3	4
Naphtha, % of total feed based on naphtha	100.0	100.0	100.0	100.0
Distillation:				
Initial, °F	99	104	160	158
10%, °F	150	162	236	255
50%, °F	242	261	324	325
90%, °F	366	410	407	380
E.P., °F	423	450	446	426
Gravity, A.P.I	61.6	58.7	51.8	51.3
Outside gas, % of total feed based on naphtha	100.0	100.0	90.9	170.5
Analysis liquid volume, %				
H_2	.....	.....	36.5	30.2
Methane	0.6	2.6		
Ethane	2.9	19.9	13.6	18.6
Ethene	0.2	0.5	2.8	3.0
Propane	12.5	38.6	24.0	19.4
Propene	2.7	5.9	8.7	10.2
Butanes	74.3	35.5	7.5	8.3
Butenes	6.6	2.9	4.8	6.7
Pentanes	0.2	0.1	1.7	3.6
Total olefins, volume, %	9.5	9.3		

the cracking tendency tends to overcome the polymerization tendency and the amount of olefin gases formed increases.

In general, the Gas Reversion process operates in the gas conversion section of the furnace at temperatures from 1020 to 1120°F. and in the naphtha reversion section at 960 to 1060°F. The outlet pressure from the furnace varies from 1,500 to 2,200 lb. per sq. in. In the Polyform process the temperatures

normally range from 1025 to 1125°F. and the outlet pressure around 1,000 to 2,000 lb. per sq. in. The pressures are maintained above the critical so that the material within the tubes is of constant physical composition. This eliminates excessive coking, which would be caused by segregation of the heavier liquid phase on the tube surfaces.

Reaction Time.—The reaction time or time of residence of the charge stock in the furnace depends upon relatively the same factors as listed above. In addition, temperature has an important effect. Within certain limits temperatures and reaction times are interchangeable in respect to yield of gasoline. High temperatures and low reaction times, or long reaction times and low temperatures, give approximately the same yields. Long times and high temperatures tend to increase the formation of aromatics.

The ability of the various hydrocarbons to resist decomposition (or their refractory ability) varies. At a given temperature, propane requires about four times the reaction time that is necessary for butane. The higher hydrocarbons, such as those found in naphtha, require less time than butane. Therefore, an optimum reaction time has to be established for each charge composition to obtain the reaction of a major proportion of the C_3 and C_4 gases without excessive cracking of the heavier naphtha which results in coke formation. Although no data are available on the reaction times used in commercial installations, it is probable that they may range from 1 to .5 min. on regular operation and higher for the production of aromatic-type fuels.

YIELDS.—The yields obtained in the Gas Reversion and Polyform process are dependent upon the charging stock and the operating variables. The refractory characteristics of the naphtha and the proportion of C_3 and C_4 hydrocarbons determine, within a certain range, the operating conditions. For a given temperature and pressure, a longer reaction time gives increased gasoline yields. For a given reaction time, higher temperatures increase the yield. With other conditions remaining constant, higher pressures increase the ultimate yield of gasoline because under higher pressures the polymerization and alkylation reactions are accelerated. Beyond certain limits at a given pressure and reaction time, higher temperatures increase the formation of cyclic compounds and their dehydrogenation to

aromatics.   This leads to condensation of the aromatics forming tar and eventually coke, which reduces the yields obtainable.

In the Polyform process, yields of 400 E.P. gasoline, stabilized to 8 to 10 lb., Reid vapor pressure, range from approximately

TABLE 5-V.—YIELD AND QUALITY OF PRODUCT DATA ON POLYFORM AVIATION FUEL

	Naphtha	Poly-formed distillate	Aviation gasoline	Safety fuel
Volume, % distillate...............	......	100.0	39.2	35.3
Acid heat, °F....................	2	68	10	2
Aromatic content, %:				
Benzene, %....................	......	4.4		
Toluene, %....................	......	10.7		
Xylene, %.....................	......	11.6		
Total, %....................	......	26.7		
Aniline point, °F.................	136	37.1		
Freezing point, °F................	......	......	....	−76
Gravity, A.P.I...................	47.5	49.8	55.8	36.2
Gum, copper dish, mg./100 cc.....	......	187	1	
Gum, oxygen, mg./100 cc.........	......	219	1	
Oxygen stability, 212°F. min......	......	105	300+	
Octane No., C.F.R.-A.S.T.M......	47	82	77	80
+1 cc. T.E.L./gal..............	57	86	84	86
2 cc. T.E.L./gal..............	......	88	88	87
3 cc. T.E.L./gal..............	66	90	90	88
Sulfur, %......................	0.05	0.04	0.011	0.018
Vapor pressure, Reid, lb..........	......	10.0	6.2	
Distillation, A.S.T.M.:				
Initial, °F....................	266	86	114	301
10%, °F.....................	290	139	156	311
20%, °F.....................	296	......	170	314
50%, °F.....................	311	245	205	326
90%, °F.....................	372	362	250	372
E.P., °F.....................	431	448	307	426

65 to 85 per cent by volume based on the naphtha charged with no outside gas added.   If outside gas is utilized, the range is from 100 to 145 per cent.   With outside gas feed, in the Gas Reversion process, the yields available show a range of 120 to 135 per cent based on the volume of naphtha charged.   These yields are variable and depend on the type of operation used.

In the manufacture of aviation fuel, the yield of distillate from polyforming or gas reversion is less than for regular gasoline production since the operation normally is adjusted to the greater formation of aromatic compounds and the reduction of the olefin content of the gasoline fraction.

Aviation fuel base made from polyform or gas-reversion distillate must be treated (usually acid treated) in some manner to reduce further the olefin content. Table 5-V gives yield and quality data on an aviation-fuel base produced from a polyform distillate.

These gasolines were produced by first rerunning the distillate into a light and heavy fraction. The light fraction was acid-treated (cold) with 20 lb. of 98 per cent H_2SO_4 per barrel, and rerun to aviation gasoline boiling range. The heavy cut was treated with 5 lb. of 98 per cent H_2SO_4 per barrel and rerun to safety fuel specifications.

QUALITY OF PRODUCT.—The distillate formed in the process under discussion is unsatisfactory as an aviation fuel or aviation-fuel base, owing to its unsaturated hydrocarbon content. This gives rise to instability and gumming, and the acid heat specifications are not complied with. However, with sufficient treatment, fuels having the characteristics shown in Table 5-V may be produced. These fulfill the necessary specifications.

COMMERCIAL APPLICATION.—In 1942 twelve large-scale plants had been built using the Polyform and Gas Reversion processes. The capacity of these plants ranged from 3,000 to 22,000 bbl. per day.

Isomerization

Recently, catalytic isomerization has been applied to the production of aviation-fuel base stocks as well as to the production of isobutane (see page 124). It has been known that isomerization takes place under certain operating conditions in thermal and catalytic processes, but until recently, no methods for the particular purpose of isomerizing mixtures of straight-chain hydrocarbons have been in commercial use. Little information is available concerning these processes other than general descriptions. The Universal Oil Products Co. (U.O.P.) is licensing and the Standard Oil Co. of Indiana is said to be operating

isomerization processes that produce isomates suitable for aviation-fuel base stocks. Also, the Phillips Petroleum Co. has recently announced a new catalytic isomerization process called *Isoversion* which may be used to produce aviation base stocks and hydrocarbons necessary for the production of high-octane fuels.

U.O.P. Naphtha Conversion.[14,15,16]—In this process the conversion of normal hydrocarbons to isohydrocarbons is effected by passing a light-debutanized straight-run gasoline in the liquid phase over a solid aluminum chloride catalyst at low temperatures and pressures. The charging stock must contain no aromatic or olefinic constituents since they sludge the catalyst. The product consists mostly of isopentanes, isohexanes, and some isoheptanes. The yields of usuable isomate are claimed to be around 98 per cent, with the 2 per cent being mostly lighter hydrocarbons. The octane number of the isomate varies with the charging stock, and usual results indicate an increase of from 18 to 20 octane numbers. The character of the isomate stock makes it valuable as an aviation-fuel blending stock.

Standard Oil Company (Indiana) Isomate Process.[14]—The Standard Oil Co. of Indiana has developed an isomerization process designed to increase the octane number of light straight-run paraffinic naphthas by conversion of the *n*-hydrocarbons to isocompounds.

No data are available on the catalyst used or the type of flow. The charging stock may consist of any debutanized cut from a straight-run or casing-head gasoline. The relative proportion of normal and isocompounds is not important. The charge is treated at temperatures under 300°F. and produces a 98 per cent yield of isomate. No gas (methane, etc.) results. The catalyst (aluminum halides) apparently has a long life under these conditions since runs of 750 hr. without shutdown have been made.

The product (isomate) contains relatively large amounts of neohexane. It may be produced with a vapor pressure of 10 lb., and it has a high-lead susceptibility. These factors make it valuable as a base blending stock for aviation gasoline. It is claimed that 62 per cent of isomate (81 octane number) may be blended with 38 per cent of alkylate (93 octane number) and 3 cc. of T.E.L. to produce an aviation fuel of 100 octane number with suitable characteristics.

Another interesting process is described in certain patents[17,18,19] in which straight-chain compounds in a straight-run naphtha are converted to branched-chain compounds of high-antiknock value. In this process the naphtha is contacted in a reaction zone with a conversion catalyst consisting of an aluminum halide, $AlCl_3$ or $AlBr_3$, and a halogen-containing promoter for the catalyst, at superatmospheric pressure and temperature, with isobutane,[17] propane,[18] or mixtures of butane, propane, and ethane.[19]   The reacting gases are free from olefins, and the pressures and temperatures are such that there is no formation of gases such as hydrogen and methane.

Catalytic Reforming

Catalytic reforming is a general term applied to processes operating in the cracking range under the influence of catalysts. It is generally referred to as *catalytic cracking*.   The reactions involved indicate that something more than cracking takes place, since the hydrocarbon molecules existing in the original charge material are not only cracked but reformed structurally.   The extent and type of reformation depend upon the conditions of operation.   This has led to the designation of *reforming* rather than catalytic cracking.

Three principal catalytic reforming or catalytic cracking processes have been developed commercially and are in use at present.   These are the Houdry process, the Fluid Catalyst process, and the Thermofor Catalytic Cracking (T.C.C.) process. Natural or synthetic clay-type catalysts are used in such processes, and the cracking and reforming reactions are carried out in the vapor phase.   The differences are primarily in operating conditions and flow of the catalyst.   The Houdry process utilizes a static catalyst and obtains continuous flow over all by alternating reaction periods and catalyst activation periods in a series of catalyst cases.   The Fluid process obtains continuous cocurrent flow by continuous reactivation and recycling of the catalyst.   The Thermofor process achieves this in much the same manner except that the catalyst flows countercurrent to the oil vapors and is continuously reactivated and recycled.

Catalytic cracking has achieved a great prominence in the refining picture since 1940.   During that year there were only 14 units operated by three companies.   These units were of the

Houdry type.   In March, 1943, the number of units had increased to 77, either already built or being built, and included not only the Houdry processes but also the Fluid Catalyst and the Thermofor Catalytic Cracking processes.   In addition several more plants were being considered at that time.   This program included 34 different companies.

The number and type of catalytic-cracking plants in operation and building as of March, 1943, are shown as follows:[19a]

Process	Built	Building	Total
Houdry...............................	16	10	26
Fluid................................	3	28	31
T.C.C...............................	0	20	20
Total...............................	19	58	77

The gasoline products from these processes may be treated satisfactorily, without great losses, so that they conform to aviation gasoline base specifications.

Catalytic Reforming, Houdry Process.[20,21,22,23,24]—The Houdry Process Corp. has developed a process in which a gasoline or naphtha can be reformed catalytically into a material of high octane number, lower sulfur content, and high lead susceptibility. This process has been in operation for some time, producing gasolines for automotive use.   It is also adapted to the production of aviation-fuel blending stock.   Recently a newer modification of the Houdry process was announced wherein the heat generated by the reactivation of the catalyst is used in the cracking reaction, thus giving more efficient operation.[20a,20b]

CHEMISTRY OF PROCESS.—The chemistry of this process is not clearly defined.   According to Sachanen,[20] the reforming reactions in general are mostly dehydrogenation, decomposition of paraffin hydrocarbons to low-molecular-weight paraffins and olefins, and various aromatization reactions.   The dehydrogenation and splitting of the paraffin molecules are cracking reactions. Aromatics may be formed by the dehydrogenation of the naphthenes and cyclization of the olefins.   Examination of the analysis of typical aviation fuels, given in a paper[21] describing the Houdry Catalytic Reforming process, shows a relatively high percentage of isoparaffins.   Thus, it would indicate that iso-

merization also takes place. The increase in octane number in this process is due to change in chemical composition, forming lighter compounds, isocompounds, and aromatics.

FLOW.—Figure 7-V shows the flow diagram for catalytic reforming applied to the manufacture of aviation gasoline. The equipment shown consists of the charge heater, the catalyst cases, the cooler for the reformed product, and the fractionation apparatus. An air heater and a turbocompressor unit are required to heat and circulate the air and gas for the regeneration of the catalyst.
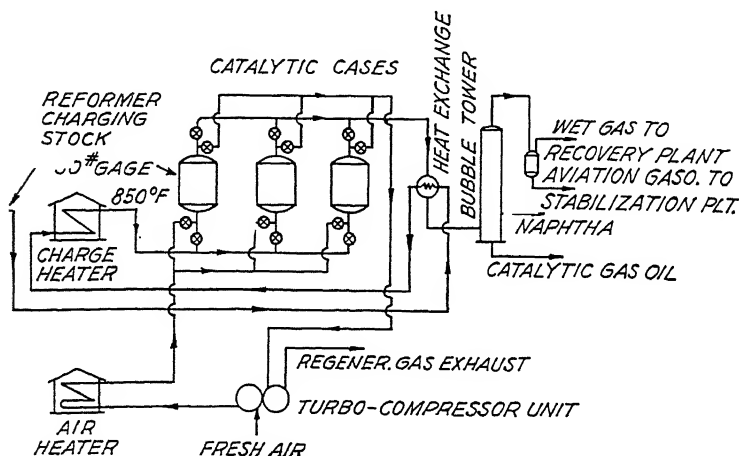

FIG. 7-V.—Flow diagram of the Houdry Catalytic Reforming process. (*Courtesy of the Refiner and Natural Gasoline Manufacturer.*)

The flow is as follows: The charging stock, consisting of either a gasoline (end point, 400 to 500°F.) or a naphtha, boiling between 250 and 500°F., is pumped through the charge heater where it is vaporized at a temperature of 850°F. The vapors pass through one of three catalyst cases, while the other two are being regenerated. The reformed products from the catalyst cases are cooled and conducted to a fractionating tower, wherein the light gases and aviation gasoline cut are taken from the top of the tower, and the heavier material from the bottom. The top stream is separated into two products: wet gas and unstabilized aviation fuel. The latter is then stabilized in a stabilizer tower.

The catalyst chambers are hooked up so that one is on stream while the catalyst in the others is being regenerated. The regeneration is accomplished by circulating controlled amounts of

air through the catalyst, which burns off the carbonaceous deposit. The exhaust gases from this combustion are utilized to drive the turbocompressor that circulates the air.

ELEMENTS OF OPERATION. *Feed Stocks.*—For catalytic reforming a wide range of feed stocks is possible. In general, gasolines having end points between 400 and 500°F. and naphthas boiling between 250 and 500°F. are used for the production of aviation-fuel stocks. The distillation range of the charging stock depends greatly on the type of crude. The more naphthenic charges may have a lower initial boiling point than the more paraffinic types: for example, naphthenic, 90 to 500°F; paraffinic, 280 to 500°F. Gas oils may also be used as charging stocks in this process. Their boiling range is determined by the crude source.

Catalyst.—The catalyst is a highly active aluminum hydrosilicate. The patents[22,23] cover the use of hydrosilicates containing 70 to 80 per cent silica, 20 to 10 per cent alumina, and not more than 10 per cent of other oxides. Iron oxide, Fe_2O_3, is not to exceed 3 per cent. Nickel oxide may be present in amounts not exceeding 10 per cent, and a manganese compound (1 per cent) may be added to facilitate regeneration. The catalyst is molded, dried, and baked in a rigid form and is arranged in the chambers to afford efficient contact with the vapors. It is also used in the form of pills or pellets approximately $\frac{1}{8}$ in. in diameter. Under the conditions of operation the catalyst becomes fouled with a deposit of carbonaceous materials. The rapidity with which the deposit forms and, coincidently, the life cycle of the catalyst depend upon the character of the charge and the conditions of operation. The time of flow through the catalyst varies from 10 to 135 min., depending upon the stock charged. The regeneration time varies from 20 to 40 min. In a description[21] of the process applied to production of aviation fuel, the times are 10 min. for reaction and 20 min. for regeneration. This permits operation of the catalyst for at least 180 stream-days before replacement.

The regeneration is carried out by burning the carbonaceous deposit off by means of a carefully controlled air stream. The temperature in this regeneration cycle should be kept below 1000°F. or the catalyst will be impaired.

Temperature and Pressure.—The temperature at which the catalytic reforming process operates depends on the stock, rate

of flow, and other conditions. The temperatures mentioned range from 850°F. on lighter charging stocks to 880°F. on the heavier ones. Pressures range from 30 to 50 lb. per sq. in. gauge.

Time of Contact.—The time of contact of the vapors with the catalyst also varies with the character of the charge. The lighter naphthas can be reformed at the rate of 2 volumes of charge (measured as liquid) per 1 volume of catalyst per hour. While for the heavier stocks, such as gas oils, the rate is lower, usually around 1 to 1. The process operates as a once-through operation and the yield drops off considerably when the residual oil is recycled.

YIELD AND QUALITY OF PRODUCT.—The yield and type of gasoline are interdependent variables. For a 400°F.-end-point gasoline of 70 octane number, the yield is correspondingly higher than that for a gasoline of 300°F. end point and an 80 octane number. Aviation fuel yields run from 80 to 60 per cent when naphthas are used as charging stocks, and 35 to 40 per cent when gas oils are charged.

Typical yields of various products made by catalytic reforming, operating to produce aviation gasoline, are shown as follows:

Gas (H_2, C to C_4)............ 13 to 15% by weight
Aviation fuel, 300°E.P....... 35 to 59% by volume (charge)
Motor naphtha............. 10 to 20% by volume (charge)
Gas oil................... 35 to 50% by volume (charge)
Catalyst deposit............ 2 to 6% by weight

When operating to produce motor fuel, the yields of gasoline are higher. Characteristics of typical aviation gasolines produced by the Houdry process are shown in Table 6-V.

TABLE 6-V.—CHARACTERISTICS OF TYPICAL HOUDRY AVIATION GASOLINE

Gravity....................	63.6	62.9	60.1	60.0
A.S.T.M. Distillation:				
Initial, °F...............	111	115	104	104
50%, °F................	196	204	212	198
90%, °F................	288	285	276	288
E.P., °F................	336	344	328	334
Acid heat. °F.............	40	28	13.5	24
Octane No. A.S.T.M. Motor.	80.6	80.1	77.6	77.7
Octane No. +3 cc. T.E.L....	91.1	92.2	90.5	92.5
Reid vapor pressure.........	6.4	6.7	7.0	7.0

These gasolines have a good lead susceptibility and, when used as base stocks for 100 octane number aviation gasoline, do not require a high percentage of isooctane blended with them.

Hydrocarbon-type analyses on aviation gasoline from paraffinic and naphthenic charging stocks are shown as follows:

Charge	Paraffinic	Naphthenic
n-paraffins, %...............	17	12
isoparaffins, %...............	63	47
Naphthenes, %...............	7	25
Aromatics, %...............	9	13
Olefins, %...................	4	3
Acid heat, °F................	20	20

The acid heat test may be reduced by a light acid treatment without lowering the octane numbers.

Commercial Application.[19a]—There were 16 Houdry units in operation in March, 1943, and 10 were being built. The 26 plants, built or building, were divided among 10 different companies.

THE FLUID CATALYST PROCESS.[25,19a]—The Fluid Catalyst process was developed by the Standard Oil Co. (N.J.), Standard Oil Co. (Ind.), M. W. Kellogg Co., the Texas Corp., Universal Oil Products Co., and Shell Oil Co., and is licensed by the M. W. Kellogg Co. and the Universal Oil Products Co. This process utilizes a cocurrent flow of finely powdered catalyst and charge vapors.

CHEMISTRY OF PROCESS.—The chemistry of the process may be considered essentially the same as that involved in the Houdry process since the conditions of operation and the catalyst types are basically somewhat the same. The principal reactions are cracking, aromatization, isomerization, and polymerization.

FLOW.—An idealized flow diagram is shown in Fig. 8-V. The flow is as follows: The gas-oil charge is vaporized in a furnace and the finely divided catalyst powder is introduced into the line carrying the vapor. The vapors and catalyst are further mixed by forcing the mixture through a perforated plate at the bottom of the reaction chamber. Catalyst and vapor pass cocurrently upward through the reaction chamber where the cracking and

conversion reactions take place. The mixture passes from the top of the reactor to a series of cyclone separators wherein the spent catalyst particles are separated from the vapors and reactivated. The cracked products are fractionated into fuel oil fractions and material boiling below 400°F. which is further fractionated in a series of towers to produce aviation gasoline stock, butane-butene fraction, and other fractions if so desired.

The spent catalyst is reactivated by passing it through a reactivating chamber cocurrently with a stream of hot air with
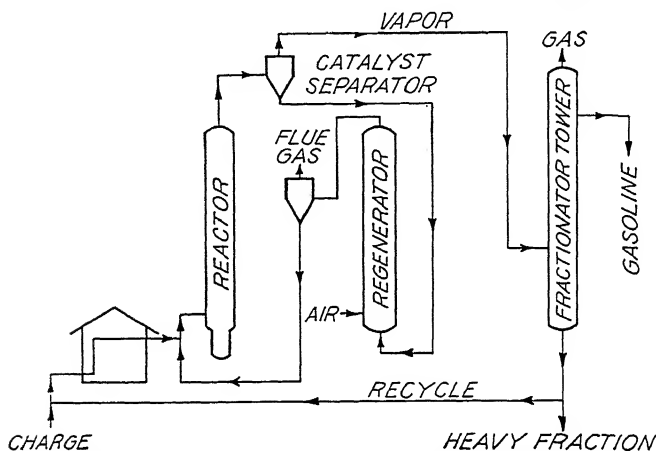

Fig. 8-V.—Schematic flow diagram of the Fluid Catalyst process.

which the carbonaceous deposit is burned off. The reactivated catalyst is then separated from the combustion gases by means of cyclone separators and a Cottrell precipitator and is recycled back into the system. The flow of the catalyst through the cracking and reactivation systems is continuous and the catalyst-vapor and catalyst-air-gas mixtures are handled as gaseous fluids.

ELEMENTS OF OPERATION. *Feed Stocks.*—The feed stocks used in this process are usually gas oils or similar distillate oils, but under certain conditions reduced crude oils may be used.

Catalyst.—The catalyst is a clay type derived from either treating natural clays or the manufacture of synthetic alumina-silica adsorbents. These materials are ground to a fine powder with the particle sizes ranging from 300 mesh to smaller for use in this process. The catalyst becomes fouled with a carbonaceous deposit as it passes through the reaction chamber, and after

separation from the vapors it is passed cocurrently with a stream of hot air through the reactivator where the deposit is burned off at a temperature of 1000 to 1150°F.

Temperature and Pressure.—The temperature of operation in this process ranges from 800 to 975°F. and the pressure is held at 10 to 15 lb. per sq. in.

YIELDS AND QUALITY OF PRODUCT.—Under normal operation, the following products are recovered: fuel oils, light and heavy, a motor-gasoline fraction boiling from 300 to 400°F., and aviation-gasoline fraction boiling from 100 to 300°F., a fraction containing C_3, C_4, and C_5 hydrocarbons, and gas containing C_1 and C_2 hydrocarbons. The aviation-gasoline cut when leaded with 4 cc. of tetraethyl lead will average 92 to 97 octane number. The C_3 to C_5 fraction will contain propane, propene, butane, isobutane, butene, isobutene, and isopentane and most of these compounds are suitable for charge materials to polymerization and alkylation processes.

COMMERCIAL APPLICATION.[19a]—Three fluid catalyst units were in operation in March, 1943, and 28 more were being built making a total of 31 units. These were distributed among 20 different companies. In addition several other units were under consideration.

The Thermofor Catalytic Cracking Process (T.C.C.).[25,25a,25b]— The Thermofor Catalytic Cracking process was developed by the research staff of the Socony-Vacuum Oil Co. The process utilizes continuous flow of catalyst and charge through reactor units with continuous reactivation of the catalyst. The catalyst flows countercurrent to the oil vapors in the reactor and counter-current to the air in the reactivator. The name *Thermofor* is derived from the clay-burning kiln[26] which is used for reactivation of the catalyst.

CHEMISTRY OF PROCESS.—The chemistry of the reactions encountered in this process may be assumed to be similar to that in the Houdry and Fluid processes. The conditions are comparable and the catalysts essentially the same. Thus the reactions that take place in one could be expected to occur in the others.

FLOW.—The flow diagram is shown in Fig. 9-V. The principal equipment consists of the following: a charge-heating furnace, a reactor containing a series of baffles over which the catalyst flows countercurrent to the oil vapor, a fractionation system for the

product, a catalyst reactivator (a Thermofor-type kiln), and elevators for charging the spent catalyst to the reactivator and the reactivated catalyst to the reactor.

The flow is as follows: The charge oil is heated to the required temperature in a furnace and converted to vapor. The vapor is caused to flow countercurrently (upward) to the catalyst mass moving downward by gravity in the reaction zone of the reactor. Above the reaction zone the vapors pass into collecting flues
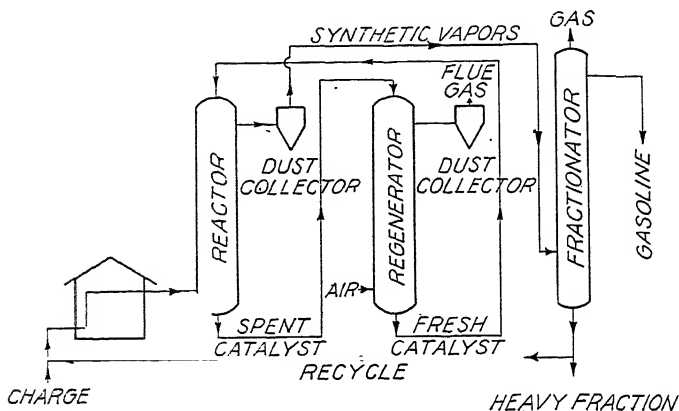

FIG. 9-V.—Schematic flow diagram of the Thermofor Catalytic Cracking process.

into the dust collector wherein the catalyst fines are separated. The vapors then pass to a fractionating system and are fractionated to the correct boiling range for motor gasoline or aviation-base gasoline.

The continuous catalyst flow is maintained in the following manner: The fresh or reactivated catalyst is charged into the hopper above the reactor. It flows from the hopper to a distributing hopper immediately above the reaction zone and from there through distributing pipes to the top of the catalyst bed in the reaction zone. The movement of the bed is downward over baffles countercurrent to the oil vapor flow. At a point below the reaction zone and below the oil vapor inlet is the purging zone, which is also equipped with baffles. The spent catalyst flows over these countercurrent to superheated steam vapors which completely remove all oil vapors. From the bottom of the reactor the spent catalyst flows to a conveyer which takes it to

the top of the reactivation kiln.   In the kiln the catalyst flows by gravity downward over baffles countercurrent to the air stream which enters at the bottom.   The temperature of combustion is controlled by circulating some cooling medium, such as steam, through finned tubes running vertically through the burning zone in the kiln.   The reactivated catalyst is withdrawn from the bottom of the kiln and conveyed to the reactor supply hopper.

ELEMENTS OF OPERATION.   *Feed.*—The feed stock may consist of a wide variety of materials when running for production of motor gasolines.   Distillate stocks of the gas-oil type are generally used.   For the production of aviation-fuel base, reprocessing of the motor gasoline formed from gas-oil cracking is carried out at low through-put rates.

Catalyst.—The catalyst used in this process is a clay alumina-silica type having flow characteristics similar to the percolation clays.   The particle size may range from 4 to 60 mesh and the pellets may be formed from extrusion of powdered material or from the crushing of large masses.   This catalyst is cheap, being formed from natural clays, and has the required flow characteristics, a low attrition rate, and a high catalytic activity. The attrition rates for this catalyst are claimed to be less than 1 lb. of catalyst per barrel of charge to the reactor.   (*Attrition rate* means the rate at which the catalyst is powdered to the point where it leaves the system with the oil vapors or the flue gases.)

.The reactivation is carried out at temperatures ranging from 700 to 1100°F.   Care must be taken to prevent excessive reactivation temperatures since the catalyst will sinter and lose its activity under those conditions.

In the early part of 1943 a new synthetic catalyst was introduced for use in the Thermofor process and Houdry process. This is called a *synthetic bead* type because it is in the form of porous spherical particles approximately $\frac{1}{7}$ in. in diameter resembling glass beads.   It has an average load-carrying capacity of 200 lb. before crushing and will carry a load of about 3,000 lb. in a packed column.   It is highly resistant to attrition and there is very little breakage.   It is very active catalytically, being equal to or better than the conventional synthetic catalysts and has a predicted life of 1 year in service in a regular T.C.C. unit. The life will vary with the operating conditions and charging

stock. Reactivation is achieved in the same manner as that for the regular clay type of catalyst.

Temperature and Pressure.—The operating temperature range for this process is given as 750 to 950°F. Presumably the lower temperatures are used for cracking or reforming gas oils while the higher temperatures are used in processing the naphtha cut for the production of aviation-gasoline base. The pressure range is given as 10 to 15 lb. per sq. in.

Reaction Time and Other Conditions.—The reaction time expressed in terms of space velocity (ratio of volume of liquid oil to apparent catalyst mass in reaction space per hour) is given at 0.2 to 3.0 volumes of oil per volume of catalyst per hour. The ratio of catalyst to oil ranges from 1.0 to 8.0. The percentage by weight of steam to weight of oil charge ranges from 0 to 20. (The steam is used to purge the oil vapors from the spent catalyst.)

YIELDS.—Yields of motor gasoline depend upon the type of stock charged and the conditions of operation. From the cracking of gas-oil stocks and using the original type of catalyst, once-through operation produces 35 to 45 per cent gasoline, based on charge stock volume, and 50 to 60 per cent with recycling.

Aviation gasoline yield data are not given for this process. It is stated, however, that the second pass operation, in which the motor naphtha cut is used as charge oil, yields 80 to 95 per cent of the aviation cut present in the motor gasoline.

This process produces aromatic compounds such as benzene, toluene, and the xylenes in recoverable quantities. Butylenes up to 8 per cent by volume of the charge can be produced with 2 to 5 per cent of isobutane. The C_3 and lighter gases are high in olefin content.

With the use of the new bead catalyst, the yields of aviation gasoline are said to be increased from 13 to 30 per cent, depending upon the characteristics of the charging stock. The increased yields based on charging stock are claimed to be as follows:

Charging Stock Base	Increased Yield %
Mixed base	13
Naphthenic base	25
Paraffinic base	30

QUALITY OF PRODUCT.—The motor gasolines range from 77 to 84 octane number (Research method), have good stability char-

acteristics, and have fairly good lead susceptibilities.   Table 7-V gives approximately the range of properties of aviation gasoline made from this process.

TABLE 7-V.—PROPERTIES OF AVIATION GASOLINE—2 PASS
T.C.C. OPERATION

Acid heat, °F.................................... 10 to 25
Aromatics, %................................... 20 to 30
Gum accelerated, mg./100 cc..................... 3 to 5
Octane number (A.F.D.1-C) clear................ 77 to 80
    +3 cc. T.E.L./gal............................ 92 to 95
    +4 cc. T.E.L./gal............................ 94 to 97
% by volume of alkylate to make 100 octane number
    fuel* (+4 cc. T.E.L.)......................... 22 to 45
Reid vapor pressure.............................   7.0

* This gasoline complies with the combustion specifications.

The quality of the aviation gasoline produced with the bead catalyst is claimed to be higher than that produced by use of the original catalyst by 23 to 35 per cent, based on power-output ratings.

COMMERCIAL APPLICATION.[19a]—In the early part of 1943 no commercial sized units using the T.C.C. process had been built. However, 9 different companies were building 20 different units, and more were being considered.

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MANUFACTURE OF HIGH-ANTIKNOCK HYDROCARBONS

In Chap. V the manufacture of base stocks suitable for blending finished aviation fuels was discussed. In reviewing the type and characteristics of base stocks available from natural and conversion sources, we found that such base fuels blended with tetraethyl lead alone would not meet the octane number specifications established for the higher grade aviation fuels such as the 91 and 100 octane grades. In many instances, however, the lower grade aviation fuels may be made in this manner.

It must be remembered that such statements apply to the general consideration of all methods, both conversion and physical separation methods, for the production of suitable base fuels. There may be and probably are exceptions. Admittedly, it would be physically possible to fractionate a suitable straight-run naphtha to procure pure hydrocarbons of the requisite characteristics and likewise possible to adjust operating conditions of certain conversion processes to produce suitable 100 octane aviation gasoline. However, in nearly all cases such practice is not economically feasible owing to high cost and low yields obtainable.

NECESSITY FOR HIGH-OCTANE BLENDING MATERIALS

Since it is usually impossible from a practical standpoint to make an aviation fuel by the simple expedient of adding a knock-suppressing agent such as tetraethyl lead to a single base stock, other means of increasing the octane number of the fuel have to be used.

There are several possible ways in which this may be accomplished and these are listed as follows:

1. Increase the lead susceptibility of the base stock by the addition of compounds, hydrocarbons or others, which will lower the lead requirement to within the specified amounts.

2. Increase the lead susceptibility by removing sulfur compounds if they are present. (This is effective for only small

changes in octane number, 1 to 3, since the specifications call for not more than 0.05 per cent sulfur.)

3. Increase the octane number of the fuel by blending a fuel compound or mixture of compounds having extremely high-octane numbers.

4. Increase the octane number by addition of a compound or compounds having high blending octane values. This point, at first thought, would be the same as the preceding point. However, this is not necessarily true since some compounds having clear (unblended) octane numbers of the order of 80 to 90 when blended in quantities of 20 to 40 per cent will have blending octane numbers of 120 to 130.

5. Achieve the highest octane number possible in the base by keeping the volatility at its highest point and still fulfill the specifications of vapor pressure and distillation range. Since the specifications covering volatility of the finished aviation fuel are extremely rigid, only small improvement can be made by varying the characteristics within the limits possible.

All the practices given above are in use in the manufacture of aviation fuel. Sulfur removal and volatility adjustment are effective for only slight improvement. The method of increasing the lead susceptibility by the addition of suitable compounds is practiced to some extent and is effective within certain limits. Since the character of the base material normally influences the lead susceptibility of the blend to a much greater extent than the added compounds, the net result is limited.

In present-day practice the methods used to bring the octane number of the base up to that required for the finished fuel are (1) the addition of high-octane compounds such as isooctane and isooctane mixtures, isoheptanes, isohexanes (neohexane), and isopentane and (2) the addition of compounds whose blending octane numbers are sufficiently high to enable a relatively large increase in octane number of the blend when small percentages are added. Such compounds consist mainly of substituted benzenes (toluene, the xylenes, ethyl, propyl, isopropyl, and butyl benzenes) and certain of the saturated cyclics such as cyclopentane and cyclohexane.

Certain alcohols and ethers have been used because of their high-octane ratings. However, this practice has not been followed generally because the heats of combustion of this type

of compound are lower than is desired.   They are partly oxidized hydrocarbons and the addition of oxygen to the hydrocarbon molecule lowers the combustion value.

TABLE 1-VI.—PROCESSES FOR THE MANUFACTURE OF HIGH-OCTANE HYDROCARBONS

Process	Molecular change	Charge materials	Direct products	Finished products
Polymerization:				
A. Catalytic.	Size and structure	Butene, isobutene	Isooctenes	Isooctanes
B. Catalytic.	Size and structure	Propene, butene, isobutene	Isoheptenes, isooctenes	Isoheptanes, isooctanes
Alkylation:				
A. Catalytic.	Size and structure	Isobutane, butene	Isooctane	Isooctane
B. Catalytic.	Size and structure	Isobutane, butene, propene	Isooctanes and isoheptanes	Isooctanes and isoheptanes
C. Catalytic.	Size and structure	Benzene, propene	Isopropyl benzene	Isopropyl benzene
D. Thermal..	Size and structure	Ethene, isobutane	Isohexane ("neohexane")	Neohexane
Isomerization:				
A. Catalytic.	Structural	Pentane, hexane, heptane, octane	Isopentane, isohexane, isoheptane, isooctane	Isopentane, isohexane, isoheptane, isooctane
Aromatization:				
Catalytic or thermal.	Structural	Hexane, hexene, heptane, octane, nonane	Benzene, benzene Toluene, ethyl benzene, propyl benzene	Benzene or substituted benzenes, toluene, ethyl benzene, propyl benzene
Cyclization:				
Catalytic or thermal.	Structural	Pentane and heavier Hexane and heavier	Cyclopentane, cyclohexane	Cyclopentane, cyclohexane

Some of the compounds occur naturally in such a combination and quantity that they may be recovered by physical (distillation and extraction) methods. Isopentane, for example, may be recovered from natural gasoline and light naphthas while toluene and certain other substituted benzenes may be recovered economically from coal-distillation processes.

In general, however, these compounds and particularly the six-, seven-, and eight-carbon-atom isoparaffins are not economically available from the usual sources, and the attention of the industry has been turned toward their synthesis by chemical conversion methods.

GENERAL CONVERSION METHODS

In commercial practice there are two methods of attack in the production of high-octane compounds. One is the combination of suitable small hydrocarbon molecules to form larger molecules having the desired characteristics, and the other is the rearrangement of the structure of hydrocarbon molecules without changing their size (based on the number of carbon atoms contained).

Under the first method we have polymerization and alkylation. Under the second, we have isomerization, aromatization, and cyclization. In order to define these methods more clearly, Table 1-VI was devised.

In studying this table it is found that the charge materials for the combination processes, polymerization and alkylation, consist essentially of the following compounds:

```
Olefins or alkenes:
   Ethene
   Propene
   Butenes
   Isobutene
Paraffins or alkanes:
   Isobutane
   Propane
Aromatics:
   Benzene
```

For the rearrangement processes the charge materials are composed of the following:

Paraffins or alkanes:
  Pentane
  Hexane
  Heptane
  Octane
  Nonane
  Some iso-C_7 to C_{10} compounds.

AVAILABILITY OF COMPOUNDS NECESSARY FOR CONVERSION PROCESSES

Olefins.—In crude oils there is little, if any, natural occurrence of the lighter olefins in which we are interested. This is less true of the heavier molecules. Apparently the lighter hydrocarbons, C_1 to C_5, were formed under conditions that saturated the carbon structure with hydrogen. Thus, recovery of such compounds from crude oil is eliminated.

When hydrocarbon oils are subjected to cracking conditions, as the term implies, there occurs a cracking of the molecules, with the resulting compounds having an insufficient hydrogen supply to saturate them. Thus, olefins are formed, and in this manner it is possible to procure all the different types of light olefins necessary for subsequent conversion.

A statistical survey of the gas production available to the refining industry in 1939 was made by Egloff.[5] This is shown in Table 2-VI.

TABLE 2-VI.—COMPOSITION OF GASES AVAILABLE TO THE REFINING INDUSTRY (U.S.) IN 1939

	Natural gas	Refinery gas, crude distillation	Cracked gas
Methane, %	69	61	53
Ethane, %	14	21	15
Ethene, %	..	..	6
Propane, %	9	12	5
Propene, %	..	..	13
Butanes, %	5	4	2
Butenes, %	..	..	6

These percentages are averages based on total production. Actual analyses of the gases in particular refineries may deviate

widely from these results. However, these may be used to compare the variation in gas composition from different sources. The butanes include n- and isobutane, and the butenes include n- and isobutene.

This source is a very valuable one and is being utilized extensively. However, in some cases the proportion of the needed compounds in cracking-process gases and also their quantity are insufficient for the conversion-process requirements. This is particularly true of ethene, butene, and isobutene, and processes have been developed for their production from plentiful and available hydrocarbons such as ethane, propane, and butane. Table 3-VI gives a general outline of the processes used in the manufacture of olefins to serve as charge materials for conversion.

TABLE 3-VI.—PRODUCTION OF LIGHTER OLEFINS

Process	Charge material	Direct product	Process in which used	Final product
Dehydrogenation: Catalytic........	Isobutane	Isobutene	Catalytic polymerization	Isooctanes
	Butane	Butene	Catalytic alkylation	Isooctanes
	Butane	Butene	Catalytic polymerization	
Thermal........	Ethane, propane, butane	Ethene, propene, butene	Thermal alkylation	Neohexane, isoheptenes

Paraffins.—The paraffins needed for both the production of olefins and the production of high-octane blending materials are ethane, propane, butane, isobutane, pentane, isopentane, hexane, heptane, octane, and nonane. Ethane, propane, butane, and pentane are recovered and separated without any great difficulty from crude oils and natural gasolines. Isopentane is also recoverable from natural gasoline in quantities usually sufficient for process needs, although in some cases it is necessary to resort to conversion to supply the necessary quantity of this hydrocarbon. The higher compounds from C_6 to C_9 are usually not separated but are converted in the proportions that they occur naturally, by a conversion process capable of changing their structure to the type desired.

Isobutane is needed in excess of its availability from usual sources such as cracking process gas and natural gasoline.   It may be produced in quantity by catalytic isomerization of butane.

TABLE 4-VI.—PRODUCTION OF ISOBUTANE

Process	Charge material	Direct product	Process in which used	Final product
Isomerization: Catalytic.............	Butane	Isobutane	Catalytic alkylation	Isooctanes
	Butane	Isobutane	Thermal alkylation	Neohexane

Aromatics.—The aromatic compound, benzene, is available commercially from two principal sources.   It is recoverable in relatively large quantities from the products resulting from the destructive distillation of coal and also from close fractionation of the product (produced under special conditions) produced by the aromatization of petroleum oils.

ADDITIONAL PROCESSING OF CONVERSION PRODUCTS

With the exception of polymerization, the processes outlined above yield products that may be utilized directly in the blending of aviation fuel or in the processes manufacturing such products.   In polymerization, however, isooctenes and isoheptenes are produced which require further processing to make them suitable blending components.   As isooctenes and isoheptenes they are monoolefins and have a deficiency of hydrogen in their structure, which makes them relatively unstable.   Their unblended octane values are lower than the corresponding saturated isooctanes and isoheptanes.   Thus, mainly because of

TABLE 5-VI.—PRODUCTION OF ISO-ANES FROM ISO-ENES

Process	Charge material	Direct product	Final product
Hydrogenation: Catalytic..................	Isooctenes Isoheptenes	Isooctanes Isoheptanes	Isooctanes Isoheptanes

their unstability, hydrogenation must be resorted to before they can be used in aviation-fuel blends. Table 5-VI describes the process.

FLOW OUTLINES OF METHODS USED FOR HIGH-OCTANE HYDROCARBON MANUFACTURE

We have discussed the individual processes that produce a finished product or materials used in the manufacture of a finished product. We are now ready to consider the whole processing picture which shows the relationship between various primary and secondary processes, used singly or in combination, to produce a desired high-octane hydrocarbon or hydrocarbon mixture.

MANUFACTURE OF ISOOCTANES

One of the more important group of hydrocarbons utilized in the manufacture of aviation gasoline is the isooctane group.
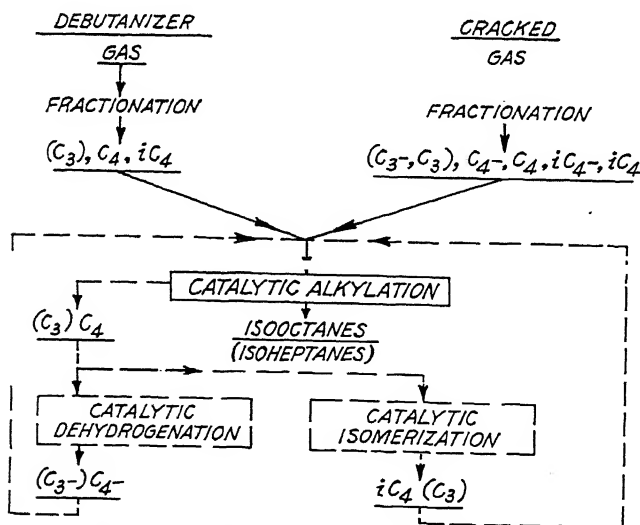
FIG. 1-VI.—Schematic flow in catalytic alkylation.

The flow outlines in Figs. 1-VI–2-VI are given to show the methods used in their manufacture.

The shorthand designation of compounds is explained as follows:

C_3 propane
C_3^- propene
C_4 n-butane
C_4^- n-butenes
iC_4 isobutane
iC_4^- isobutene

The parentheses around certain compounds indicate that they may or may not be included in the feed to the process. The
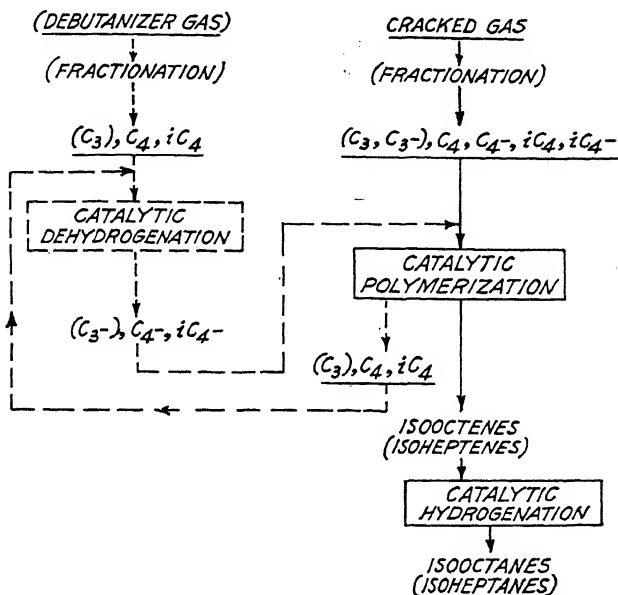
CATALYTIC POLYMERIZATION

Fig. 2-VI.—Schematic flow in catalytic polymerization.

dotted flow lines and boxes around some of the processes indicate that they may be used if necessary to increase the proportion of one or more components in the feed. The flow outlines shown here are idealized. In commercial practice many modifications are used which cannot be shown satisfactorily in this type of diagram.

Manufacture of Neohexane

Another important high-antiknock-value compound suitable for blending in aviation fuel is one of the isohexanes, neohexane

or 2,2-dimethyl butane. This hydrocarbon is produced commercially by the Thermal Alkylation method.

MANUFACTURE OF ISOPENTANE

According to present practice in the manufacture of aviation fuel, isopentane has an important dual role. It is used as a high-octane blending component and also as an agent to bring the finished fuel to the correct vapor pressure.
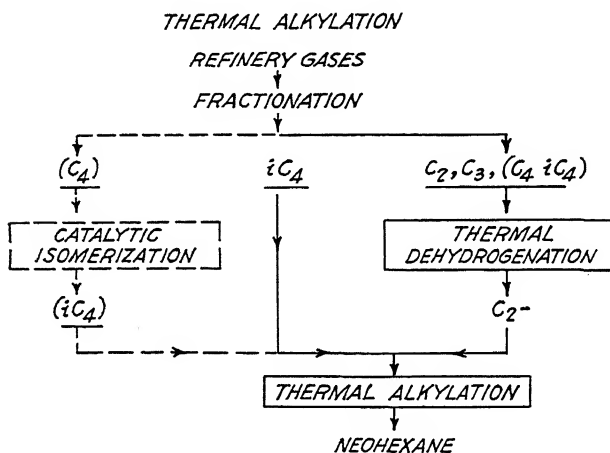

FIG. 3-VI.—Schematic flow in thermal alkylation.

Isopentane is available to some extent in most crude oils and natural gasolines. From crude oil the average yield is not over 0.5 per cent[1] and that from natural gasoline probably does not average over 16 per cent.[1] Although in some cases sufficient isopentane may be available for aviation-fuel production, in others, conversion must be utilized to secure the amount required.

A method[1] of recovering isopentane from crude oil or natural gasoline is shown in Fig. 2-V. The feed to the primary stabilizer consists of either the distillate from a crude oil topping tower or unstabilized natural gasoline. The overhead product from the primary stabilizer is propane and lighter gases. The side-draw stream taken from several adjacent plates consists of a butane-pentane mixture and the bottoms from the tower repre-

sent stabilized naphtha or natural gasoline. The side-draw stream is further fractionated in a secondary tower to produce light gases overhead, butane mixture from near the top of the tower, isopentane from a point below the feed inlet, and heavier material from the bottom. This is recycled into the primary stabilizer at a point below the initial feed.

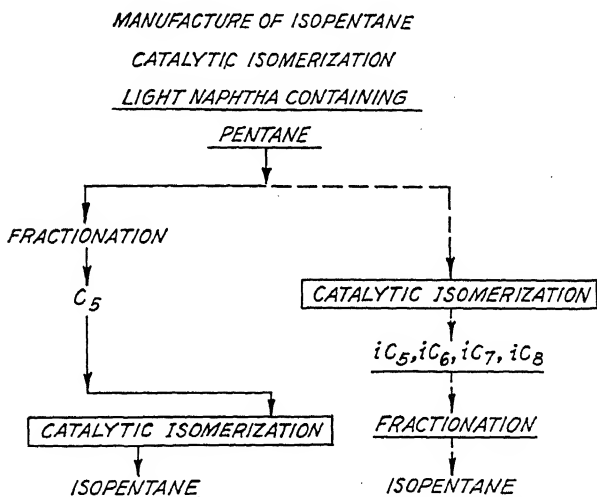This method is one of many distillation-fractionation flow methods for the production of isopentane. There are many

FIG. 4-VI.—Schematic flow in the manufacture of isopentane by catalytic isomerization.

possible ways and the one used depends greatly upon the existing fractionation equipment in the refinery or natural gasoline plant.

When it is necessary to resort to conversion to supply an adequate amount of isopentane, catalytic isomerization may be used as shown in Fig. 4-VI.

Another type of compound (the alkylated benzene or substituted aromatic) having high antiknock value and excellent blending octane properties is being considered for commercial-scale production in the refinery industry, and one of these, isopropyl benzene (or cumene), is known to be under production at the present time. The process utilized is said to be a catalytic polymerization process producing cumene from benzene and propene.
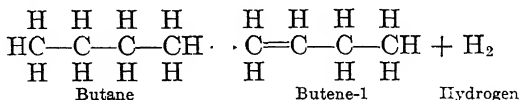
COMMERCIAL PROCESSES IN THE MANUFACTURE
OF HIGH-OCTANE COMPOUNDS

We have discussed the processing and the relationship of the various conversion methods from a general standpoint. In the following pages are described the actual processes in use in the refining industry for the production of individual or groups of specific high-antiknock-value compounds. Both primary and secondary processes are included and are arranged in the following order:
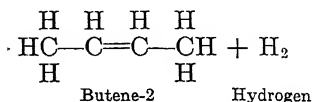
1. Production of olefins:
    a. Catalytic dehydrogenation
    b. Thermal dehydrogenation
2. Production of primary isoparaffins:
    a. Catalytic isomerization
3. Production of finished high-octane compounds:
    a. Catalytic alkylation
    b. Thermal alkylation
4. Production of isoolefins to be converted to finished high-octane compounds:
    a. Catalytic polymerization
5. Conversion of isoolefins to isoparaffins:
    a. Catalytic hydrogenation

DEHYDROGENATION[2,3,4]

Dehydrogenation is the process in which the hydrocarbon or mixture of hydrocarbons charged is subjected to conditions that cause the splitting of hydrogen from the molecules. This results in unsaturation of the structure with the formation of double bonds or double-carbon linkages. For example, butane is dehydrogenated to butene,

$$
\begin{array}{cccc}
H & H & H & H \\
HC\!-\!C\!-\!C\!-\!CH & \cdot & \cdot C\!=\!C\!-\!C\!-\!CH + H_2 \\
H & H & H & H
\end{array}
$$

Butane   Butene-1   Hydrogen

or

$$
\begin{array}{cccc}
H & H & H & H \\
\cdot HC\!-\!C\!=\!C\!-\!CH + H_2 \\
H & & & H
\end{array}
$$

Butene-2   Hydrogen

Dehydrogenation takes place in practically all cracking processes since the conditions under which cracking occurs favor

also the dehydrogenation reaction. Therefore, from a general viewpoint, cracking processes and dehydrogenation processes have a common basis for consideration. Thus, in cracking, a relatively large amount of unsaturated hydrocarbons is produced and this source furnishes considerable amounts of propene, butenes, isobutene, pentenes, and isopentenes which are of value in the manufacture of high-octane isocompounds.

In cracking, since the primary purpose of the process is to break up the larger molecules into smaller ones boiling within the gasoline range, the conditions are adjusted to bring about the scission or breaking of carbon-to-carbon linkages. This is undesirable when the stock charged consists of a saturated paraffin gas such as butane for the purpose of producing an unsaturated product such as butene without breaking any of the carbon-to-carbon bonds. Specific dehydrogenation processes are distinct from the normal cracking processes in that there is little if any rupture of the carbon-to-carbon structure of the hydrocarbon charged.

Both catalytic and thermal dehydrogenation are used in the manufacture of hydrocarbons to be utilized in the production of aviation fuel.

TABLE 6-VI.—CATALYSTS IN CATALYTIC DEHYDROGENATION

Catalyst	Reference
$Al_2O_3 + H_2O$ (trace)	1
Cr_2O_3	1
NiO	1
$Fe_2O_3 + ZnO$	1
VSO_4	1
Ni (reduced)	1
Cr_2O_3 on Al_2O_3	2
V_2O_5 on Al_2O_3	2
TiO_2 on Al_2O_3	2
$Cr_2O_3 \cdot MoO_3$	3
Cr—Cu—H_3PO_4	3

Catalytic dehydrogenation has been studied with the idea of making olefins from corresponding light paraffins for use in polymerization and alkylation processes. By dehydrogenating C_4 compounds to olefins without destruction of the C_4 molecules, high yields of material essential to the manufacture of isooctane are obtained. The catalysts investigated consist mostly of oxides of elements in the IVth, Vth, and VIth groups of the periodic
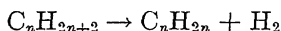
table supported on ceramic bases.   Table 6-VI lists some of those reported in the literature.

In general, the catalysts are used at temperatures of from 932 to 1382°F. and at pressures of around 1 atm.   The catalyst life is relatively short, but materials of this type can be rejuvenated by heating to 1112 to 1292°F. in the presence of air.
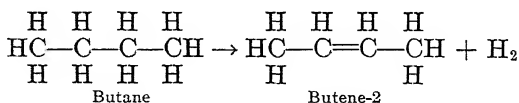
Thermal dehydrogenation is not so selective and tends to break the carbon skeleton of the hydrocarbon, forming considerable quantities of lighter molecules as well as the desired unsaturates. Temperatures in this type of dehydrogenation range from 1400 to 2200°F. and the pressures range from 5 to 50 lb. abs.

Catalytic Dehydrogenation Process (U.O.P.).[5]—The Universal Oil Products Co. has developed a Catalytic Dehydrogenation process which is claimed to be highly selective and capable of converting C_2 to C_4 hydrocarbons to the corresponding C_2 to C_4 olefins with yields approximating 90 to 95 per cent of the theoretical.   This process is used in the conversion of n-butane and isobutane into butenes as well as propane and ethane into the corresponding olefins.   The C_4 hydrocarbons are utilized in polymerization processes for the production of dimers and trimers which can be hydrogenated to form high-octane fuels. The lower olefins may also be polymerized and hydrogenated with relatively the same results.
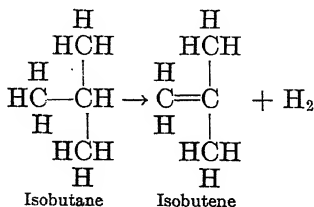
CHEMISTRY OF PROCESS.—Dehydrogenation under catalytic conditions follows the reaction

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$$

In the case of butane the reaction is

$$\begin{array}{ccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{HC} & \text{C} & \text{C} & \text{CH} & \rightarrow & \text{HC} & \text{C} & \text{C} & \text{CH} + H_2 \\
\text{H} & \text{H} & \text{H} & \text{H} & & \text{H} & & & \text{H}
\end{array}$$

<div align="center">Butane   Butene-2</div>

For isobutane,

$$\begin{array}{ccc}
\text{H} & & \text{H} \\
\text{HCH} & & \text{HCH} \\
\text{H} \; | & & \text{H} \; | \\
\text{HC}\text{—}\text{CH} & \rightarrow & \text{C}\text{=}\text{C} \quad + H_2 \\
\text{H} \; | & & \text{H} \; | \\
\text{HCH} & & \text{HCH} \\
\text{H} & & \text{H}
\end{array}$$

<div align="center">Isobutane   Isobutene</div>

The catalyst used in this conversion is a chromium oxide on alumina type.

The conversion is exothermic, *i.e.*, it is accompanied by the evolution of heat, and the catalyst chambers must be cooled for temperature control.

FLOW.—The flow diagram shown in Fig. 5-VI gives the general flow of this Catalytic Dehydrogenation process. The equipment consists of the following: heater for the butane charge, reactors containing the catalyst, cooling-compression-condensing system, separator for separating the hydrogen and light gases from the
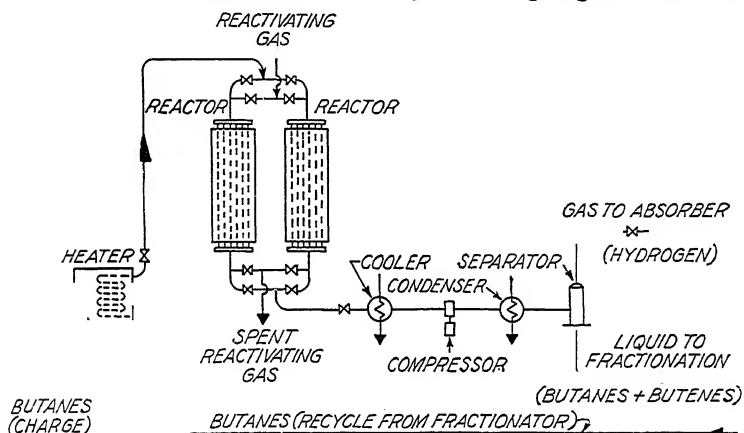
FIG. 5-VI.—Flow diagram of the Catalytic Dehydrogenation process. (*Courtesy of Refiner Natural Gasoline Mfr.*)

butane-butene liquid, and the fractionation system for separation of the butanes from the butenes.

The flow is as follows: The charge material consisting of (for example) a mixture of *n*- and isobutanes is heated in a furnace to the temperature required for the reaction in the presence of the catalyst. The heated gases then pass through one of several catalyst chambers or reactors where the dehydrogenation takes place. The reactors are of the tubular heat-exchanger type with the catalyst distributed throughout the tubes. The operation is so conducted that while dehydrogenation is being carried out in one reactor the catalysts in others are being reactivated by means of a stream of gases containing oxygen. The products from the reactor, consisting of *n*- and isobutenes, butanes, hydrogen, and small amounts of methane, ethane,

ethene, propane, and propene, are cooled, compressed, cooled again, and passed to a separator. In this separator the liquid portion, consisting mainly of butane and the butenes, are separated from hydrogen and the light gases. These light gases may be further processed to recover the hydrogen and desirable hydrocarbons. The liquid butane-butene fraction is taken to a fractionating system wherein the light gases dissolved in the C_4 fraction are separated and the butanes are separated from the butenes. The butanes are recycled into the dehydrogenation feed and the butenes are stored or sent directly to a conversion process, polymerization or alkylation, which converts them into high-antiknock hydrocarbons boiling in the gasoline range.

ELEMENTS OF OPERATION. *Feed Stocks.*—The feed to the Catalytic Dehydrogenation process may consist of ethane, propane, butane, and isobutane singly or in mixtures. If the products are intended for use in the Neohexane Thermal Alkylation process, essentially ethane and propane would be charged, and, if intended for use in catalytic selective polymerization or alkylation, mostly butanes would be charged.

Catalyst.—The catalyst consists of chromium oxide on alumina distributed in a number of tubes in the reactor or catalyst chamber through which the material to be dehydrogenated passes. During the reaction, carbonaceous materials are deposited on the catalyst, which reduces its efficiency progressively. The length of the operation cycle is therefore short—approximately 1 hr. After the efficiency is reduced to the lower limit for satisfactory operation, the gases are conducted to another rejuvenated reactor and the first is reactivated by heated oxygen-containing gases which remove the carbonaceous materials by burning. The efficiency of the catalyst is very slightly reduced by reactivation, and it has been shown to have operated effectively after 2,000 reactivations.

The catalyst is not poisoned by sulfur compounds or by carbon monoxide. Since it is, however, poisoned by iron oxides, the material used in the construction of the reactors must be such that possible contamination by iron oxides is eliminated.

Temperature and Pressure.—The temperature at which the Catalytic Dehydrogenation process operates ranges from 932 to 1382°F., and the pressure is approximately 1 atm. The exact temperature and pressure for any given operation depend on

the composition of the charging stock, the state of the catalyst, the space velocity, and the products desired.   From the literature it is indicated that the range given above covers essentially all these variables.

Time of Contact.—The contact time for this process expressed in terms of space velocity ranges at different temperatures from 500 to 10,000.   (Space velocity is defined as the volume of charge material or hydrocarbon, under the conditions specified, per unit volume of catalyst per hour.)   Data[5] given on the catalytic dehydrogenation of normal butane show that at a temperature of 1022°F. and at a space velocity of 500, the dehydrogenation is 40 per cent, while at the same temperature and a space velocity of 10,000, the conversion is 4 per cent.   At a temperature of 1112°F. and a space velocity of 500, the conversion is 67 per cent, and at a space velocity of 10,000 it is 22 per cent. At 1202°F. and a space velocity of 1,500, the conversion is approximately 83 per cent, and at 10,000 the conversion is 60 per cent.   Similar trends are shown for mixtures of *n*-butane and isobutane, and isobutane alone.

YIELDS.—The yields in this process are increased for a given temperature by increasing the contact time up to certain limits. For a given contact time, increase in temperature increases the yield.   Under optimum conditions, yields approximating 90 to 95 per cent of the theoretical are obtained.   Data[5] given on the operation of a semicommercial plant are shown in Table 7-VI.

TABLE 7-VI.—DEHYDROGENATION

Charge stock	Butane	Butane:isobutane 1:1	Isobutane (mainly)
Approximate space velocity......	1,450	1,450	1,350
Average temperature, °F........	980	1,000	1,010
Inlet pressure, lb..............	52	52	65
Outlet pressure, lb.............	18	20	5
Yield per pass (approx. mol C_4H_8/100 C_4H_{10} charge).......	25	27	23

QUALITY OF PRODUCT.—By recycling, approximately 90 to 95 per cent conversion to olefins is obtained.   The type of olefin produced is determined by the type of charge material.   This process is claimed to produce gas containing hydrogen (more than

90 per cent) which may be used to hydrogenate the olefin dimers and trimers formed in the catalytic selective polymerization process.
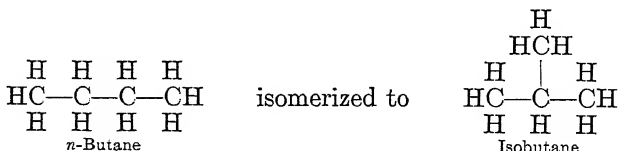
COMMERCIAL APPLICATION.—Three commercial dehydrogenation plants were constructed and placed in operation in 1940. These had a total capacity of 3,000 bbl. of butane per day. It is understood that several more are in operation and a number under construction.

Thermal Dehydrogenation.—Thermal dehydrogenation is nonselective in that the splitting of the molecules predominates the simple hydrogen separation. Therefore, when it is desired to produce, for example, butene from butane, or isobutene from isobutane, catalytic dehydrogenation is used.

In one process, where quantities of ethene are desired, thermal dehydrogenation is used. This process is accessory to that of thermal alkylation used by the Phillips Petroleum Co.* The charge in this process consists of ethane, propane, and butane; the temperature is around 1425°F.; and the pressure is a few pounds above atmospheric. These conditions favor the formation of ethene.

ISOMERIZATION

Isomerization may be defined as the alteration of molecular structure of a hydrocarbon (or other organic) compound without changing the number of carbon and hydrogen atoms in the compound. Thus, the compound, n-butane, having the structural formula shown below, may be isomerized to isobutane.

```
                                        H
                                       HCH
    H   H   H   H                    H  |  H
    HC—C—C—CH      isomerized to     HC—C—CH
    H   H   H   H                    H   H   H
       n-Butane                        Isobutane
```
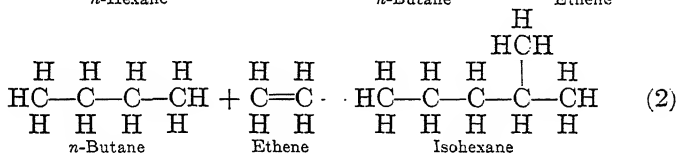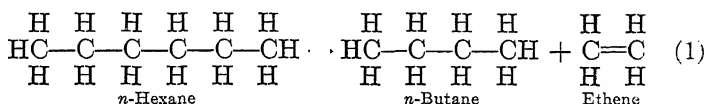
The process of isomerization has become increasingly important in the production of high-octane fuels, both from the standpoint of the production of basic materials to be utilized in the manufacture of high-octane compounds and the rearrangement of the structure of low-octane hydrocarbons to high-octane hydrocarbons which are to be used directly in the fuel.

* For a description of thermal alkylation see p 173 (Chap. VI).

It has been shown previously that the branched-chain hydrocarbons have much higher antiknock value for use as fuels than the corresponding straight-chain hydrocarbons. For example, n-hexane has an octane number of 34 while the isohexanes range from 73 to 95, the more highly branched hexanes having the higher antiknock qualities. Likewise, normal heptane has an octane number of 0 while the isoheptanes range up to 100+ octane number.

The mechanism of isomerization is not definitely agreed upon by workers in that field. Ipatieff et al.[6] in studying the isomerization of n-hexane in the presence of AlCl$_3$, HCl, and water concluded that the reaction takes place in steps as follows:

```
 H  H  H  H  H  H         H  H  H  H       H  H
 HC—C—C—C—C—CH  ·  HC—C—C—CH  +  C=C      (1)
 H  H  H  H  H  H         H  H  H  H       H  H
      n-Hexane               n-Butane       Ethene
                                            H
                                           HCH
 H  H  H  H     H  H     H  H  H  |  H
 HC—C—C—CH  +  C=C  ·  HC—C—C—C—CH        (2)
 H  H  H  H     H  H     H  H  H  H  H
     n-Butane   Ethene        Isohexane
```

Catalytic isomerization of butane, pentane, hexane, heptane, and octane, using various catalysts under varying conditions, has been reported in the literature. Table 8-VI lists incompletely the reported experimental isomerizations.

A general line-up of the catalysts used for experimental work on isomerization indicates that the activity approximately increases as follows:

$$ZnCl_2$$
$$ZnCl_2 + HCl$$
$$MoS_3$$
$$AlCl_3$$
$$AlCl_3 + HCl$$
$$AlCl_3 + CuSO_4 + HCl$$
$$AlBr_3$$
$$AlBr_3 + HCl$$
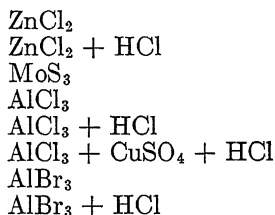
Also it is indicated that the lower hydrocarbons tend to isomerize more completely under less stringent conditions of pressure and temperature than do those of higher boiling point.

Thermal isomerization of n-octane will yield under certain conditions (1022°F.) a maximum of 9.9 per cent of isohydro-

carbons.[13] Thermal isomerization in itself is not of great importance at the present time for the production of aviation gasoline but, under certain cracking conditions, the increase in octane number of the cracked products above that expected is explained by some authorities as due to isomerization.

TABLE 8-VI.—ISOMERIZATION OF ALIPHATICS

Hydro-carbon	Catalyst	Conditions	Contact time, hr.	Yield, %	Ref.
n-Butane	$AlCl_3$, $CuSO_4$, 2HCl	Liq. phase, 158°F.	. . . . .	79	7
n-Butane	$AlCl_3$, HCl	Vap. phase, 230–356°F.	. . . . .	72 58	7
n-Pentane	$AlCl_3$, $AlBr_3$	Liq. phase, 77–194°F.	. . . . .	30–50, iC_4	8
n-Pentane	$AlCl_3$, $CuSO_4$, HCl	Liq. phase, 122–194°F.	. . . . .	15–20, iC_6	8
n-Pentane	$AlCl_3$, $AlBr_3$, HCl	Room temp.	24–36	40–58	9
n-Hexane	$AlCl_3$	. . . .	. . . . .	. . . .	10
n-Hexane	$AlCl_3$	. . . .	. . . . .	. . . .	11
n-Heptane	$AlCl_3$	. . . .	. . . . .	. . . .	11
n-Heptane	$ZnCl_2$ MoS_3	572–752°F. 788°F.	6 13	20–25	12
n-Heptane	$AlCl_3$, HCl	104°F.	5	16	13
n-Octane	MoS_3 $ZnCl_2$	824°F., 70 atm.	3 3	23.6 13.3	12
n-Octane	$AlCl_3$ (10%)	120–140°F.	1–2	31–37	13
n-Octane	Pt on C	In H_2, 572–590°F.	. . . . .	15	14
n-Octane	Ni on Al_2O_3	In H_2, 572–590°F.	. . . . .	5.5	14

Catalytic isomerization on the other hand is now being used commercially for the conversion of n-butane to isobutane and also for the conversion of light naphthas of relatively low-octane number to "isomates" of higher octane number. The former process yields material necessary for alkylation processing while the latter gives a gasoline that makes an excellent aviation-fuel base.

Other processes (see Chap. V, pages 72 to 75) recently announced will convert pentanes, hexanes, and perhaps heavier hydrocarbons to isomers of high-octane number.

Commercial Application.—At the beginning of 1943, 32 butane isomerization plants were in operation and building.[14a] This represents a total capacity of 25,500 bbl. per day. The largest unit processes 2,850 bbl. of butanes per day and the smallest 68 bbl.; the average-sized plant processes around 200 bbl. per day.

Catalytic Isomerization of Butane (Shell Isomerization Process).[15]—The first commercial Isomerization process was developed by the Shell Development Co. for the isomerization of n-butane to isobutane. Such a process is particularly valuable to the refiner using one of the alkylation processes which require a relatively large amount of isobutane.

This process is used primarily to adjust the isobutane content of the available feed stock to the Alkylation process to the desired amount. A typical butane-butene cut from a cracking unit has the following composition:

	Mol Per Cent
Isobutene	18
n-Butene	24
Isobutane	22
Butane	36

An isobutane content of at least 50 mol per cent (isobutane to butene, ratio 4:1 to 8:1 necessary in the H_2SO_4 Alkylation process) is required.

CHEMISTRY OF PROCESS.—It has been shown before that the tendency of the smaller hydrocarbons to isomerize is greater than that of the longer hydrocarbon chains. In the Shell Isomerization process butane is isomerized to isobutane in the presence of a catalyst consisting essentially of aluminum chloride supported on a porous solid inorganic material which has been partly dehydrated by heating above the temperature used in the isomerization reaction. This material may be kaolinite, bauxite, zeolite, aluminum oxide, magnesium oxide, silica, and other similar substances. In addition, anhydrous hydrochloric acid is present in the system to increase the life and activity of the aluminum chloride catalyst. The reaction is shown as follows:
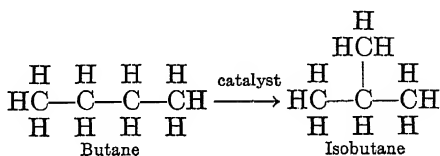
Flow.—The flow diagram shown in Fig. 6-VI is a typical flow arrangement for a butane isomerization plant.   The principal equipment for the process consists of the following: butane gas driers, heaters, catalyst vessels, coolers and condensers for the isomate, isomate receiver equipped with vent for gases, special acid-resistant charge pump for charging the isomate and HCl into the HCl stripping system, the HCl stripping column equipped
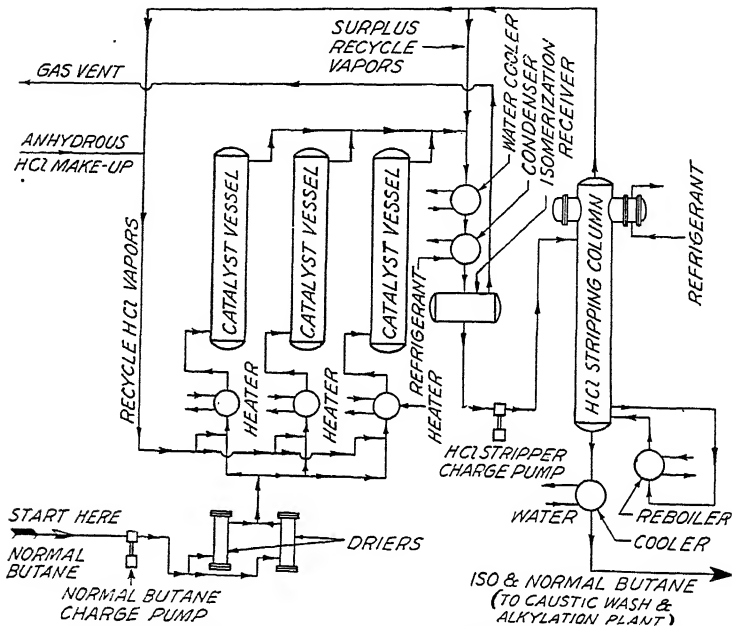

Fig. 6-VI.—Flow diagram of the Catalytic Isomerization process (Shell butane process).   (*Courtesy of Petroleum Engineer.*)

with a low-temperature refrigerated reflux condenser at the top and a reboiler at the bottom, and a fractionating system for the separation of the normal and isobutane.

The almost pure *n*-butane is charged to the isomerization system by means of a charging pump through driers which completely remove all water.   Closely controlled amounts of anhydrous hydrochloric acid are added to the dried butane and the mixture is passed through heaters which raise its temperature to that required for isomerization.

The heated mixture is passed through the catalyst vessels containing anhydrous AlCl₃ on a support composed of solid

inorganic material.   The catalyst vessels are arranged in parallel so that any one may be shut off from the rest of the system in order that the spent catalyst may be replaced without interrupting the operation of the plant.   The material flowing from the catalyst chambers consisting of HCl gas, butane, and isobutane is cooled, totally condensed in a refrigerated condenser, and passed to a receiving tank.   From this tank some of the HCl vapor is recycled into the system and the remainder of the HCl and all of the butane-isobutane is transferred through a charge pump to the HCl stripping column.   In this column the HCl is stripped from the butane-isobutane and added to the HCl recycle.   Arrangement is made for the excess HCl to be by-passed into the isomate-HCl receiving tank where it is reabsorbed in the liquid.   The column is equipped with a refrigerated reflux condenser, to ensure complete stripping, and a reboiler at the bottom.   The liquid butane-isobutane mixture is withdrawn from the bottom of the column through a water-cooled heat exchanger and then passed to a butane-isobutane fractionater. There the isobutane is separated and sent on to an isobutane receiver for use in the alkylation process, and the butane is recycled into the isomerization system.

ELEMENTS OF OPERATION.   *Feed Stocks.*—The feed stock for the Butane Isomerization process should consist of essentially pure *n*-butane.   Propane and isobutane when present are not harmful to the operation.   Olefins and pentanes above certain limits of concentration adversely affect the catalyst life.

Catalyst.—The catalyst consists of anhydrous $AlCl_3$ supported on a porous inorganic material such as partly dehydrated kaolinite, bauxite, alumina, and silica, which has been partly dehydrated at a temperature above that used in the isomerization reaction.   The anhydrous HCl is added to the system as a catalyst activator and preservative.   The amount of HCl in the system is critical and depends upon the current life of the catalyst.   Therefore, its proportion to the amount of butane charged varies and is under careful and constant control.   In a patent[17] on the process the pressure of HCl vapor is given as 3 atm.

Temperature and Pressure.—Beyond stating that isomerization of *n*-butane to isobutane takes place under mild conditions, the paper describing the process gives no definite temperatures or

pressures.   Reference again to the patents indicates a temperature range of 60 to 120°F.,[16] and under 200°F.[17]   The reaction is mildly exothermic; consequently, the catalyst can be maintained at the required temperature by utilizing this heat with little if any addition from the outside.

YIELDS.—The once-through yield is claimed to be 40 to 45 per cent conversion of the *n*-butane present to isobutane.   The theoretical yield, based on equilibrium calculations under the conditions of this isomerization, would be about 68 per cent. Continuous recycling of the *n*-butane, separated from the isobutane, into the system is claimed to give an almost complete conversion of all butane charged to the isocompound.

Although the reaction is essentially straight isomerization, in the course of time small quantities of methane and ethane formed from side reactions accumulate in the recycle HCl and have to be removed from the system.

QUALITY OF PRODUCT.—Practically pure isobutane is produced by this isomerization process.

EQUIPMENT.—Owing to the fact that the presence of water in the system would interfere with the isomerization efficiency as well as cause corrosion, owing to the formation of dilute hydrochloric acid, it is necessary to take special care in the construction of the equipment so that no water can enter.   Ordinary carbon steel is sufficiently corrosion-resistant in the absence of water.

U.O.P. Isomerization Process.[18]—The Universal Oil Products Co. has recently announced a commercial isomerization process licensed under the U.S. patents 2283142 and 2283143.   The patents are concerned principally with the conversion of *n*-butane to isobutane.   From another source[18] it is stated that conversions of *n*-pentanes, hexanes, and perhaps heavier hydrocarbons to the corresponding isocompounds are feasible.   The information given on the following pages was taken from the patents and one other source.[18]

Butane Conversion.   CHEMISTRY OF PROCESS.—The chemistry of the conversion of the *n*- to isobutanes is the same for all isomerizations.   An example of the structural change in the molecule is shown on page 44.   The reaction is mildly exothermic.

FLOW.—The process will operate under either batch or continuous conditions.   For small installations the batch process is more suitable, while for larger plants the continuous flow is

better.   From the patent the continuous flow is described as follows: The butane is pumped through a tubular heating element and heated to a given temperature and pressure.   Along the line of flow a separate or combined injection of metal salts and hydrogen halide is made and the mixture after passing through the heating element is conducted to enlarged insulated chambers where the reaction is completed.   The catalyst is separated and the products fractionated to separate the isobutane from the butane, which can be recycled.

As an alternative, the butane and hydrogen halide mixture can be passed through a converter containing heated beds of granular catalyst alone or based upon some inert material.   The products may then be fractionated and the butane recycled as above.

ELEMENTS OF OPERATION.   *Feed Stocks.*—The feed consists of essentially pure butane with practically no olefins present.

Catalysts, Operating Conditions, and Yields.—From the example given in the patents on batch operations using various catalysts and conditions, Table 9-VI was devised.   It must be remembered that these data refer to batch operation, and conditions for continuous operation may be considerably different.

In the description, the general proportions of 10 per cent by weight of aluminum chloride and 1 to 2 per cent by weight of hydrogen chloride are given.   The percentages are based on the total reactants.   The temperature range is from 176 to 392°F., and the pressure from 5 to 50 atm.   The yields claimed are from 60 to 65 per cent by weight.

The high pressures are claimed to prevent the volatilization of the granular catalysts and prevent the excessive formation of hydrogen and light hydrocarbons.

TABLE 9-VI.—BUTANE ISOMERIZATION—BATCH

Catalyst	Wgt. % of cata-lyst	Hydro-gen halide	Wgt. % hydro-gen halide	Temp., °F.	Pres-sure, atm. approx.	Time, hr.	% yield iC_4
$AlCl_3$	16.4	HCl	1.6	302	30	12	66.5
$AlCl_3$, sublimed. . .	. . . .	HCl	. . .	320	25–30	. .	63.0
$ZnCl_2$ on pumice 50-50	. . . .	. . . .	. . .	392	30	. .	60.0
BF_3	. . .	HF	. . .	356	. . . . .	. .	62.0

Corrosion will be encountered, if moisture is present, owing to the presence of HCl.   Therefore, precautions should be taken to prevent moisture from entering the system.

POLYMERIZATION

Polymerization is defined chemically as the combination of two or more like molecules to form one that is larger without loss of any atoms existing in the original compounds.   The definition of polymerization is somewhat broadened when used in connection with petroleum-conversion processes in that the term is applied to the combination of two or more similar substances forming a compound that has a molecular weight equal to the sum of those of the reacting substances.   Thus, it applies to the reaction between propene and butene, forming heptene, as well as the reaction between two molecules of butene, forming octene.

Polymerization, as used in the refining industry, refers to the combination of olefin molecules.   There are two principal methods of effecting such combinations; thermal and catalytic. Some authors[19] claim that the term *thermal polymerization* is a misnomer, since the condition under which this is effected is within the cracking range and the predominant reaction is that of cracking. However, it has been proved that polymerization does take place, the extent depending upon the reactants and the conditions.

Thermal Polymerization.[20]—Both aliphatic and cyclic olefins polymerize under thermal conditions, and the diolefins of both types show more of a tendency to polymerize than do the monoolefins.   The lighter olefins are the most easily polymerized; ethene, for example, will polymerize under less severe conditions of temperature and pressure than will propene and butene.

In commercial practice, temperatures of 900 to 1025°F. and presures around 1,500 to 2,000 lb. per sq. in. are effective in producing polymerization of the C_2, C_3, and C_4 olefins when diluted with paraffins.   It is also true that cracking takes place under these conditions.

Polymerization, using mixtures of C_2, C_3, and C_4 olefins, forms a mixture of C_4 to C_8 monoolefins, and it is probable that diolefins are formed through cracking and dehydrogenation.   Thermal polymerization does not lend itself well to selective operation

because of this cracking tendency, and therefore, it is generally considered unsuitable for the manufacture of isooctenes.

Catalytic Polymerization.[20]—The use of catalysts in polymerization enables effective olefin combination at much lower temperatures than does straight thermal polymerization. Many catalysts have proved to be effective polymerization aids. Sulfuric acid, phosphoric acid, both concentrated and dilute, zinc chloride, aluminum chloride, sulfides of heavy metals, and certain clays have been used experimentally with greater or less success.

When sulfuric or phosphoric acids are used, the mechanism of the polymerization is believed to be as follows: The olefins first combine with the acid forming an ester; then in the second stage the esters decompose, splitting off the free acids; and finally the hydrocarbon radicals combine to form polymers.

The mechanism of catalysis in the presence of the sulfide, chloride, and clay types is not clear although there have been many theories proposed.

In general, the higher olefins are more easily polymerized catalytically than the lighter.   This is the reverse of the tendency shown in thermal polymerization.

There are two types of catalytic polymerization processes in use commercially: *selective* and *nonselective* processes.   In the selective processes the feed composition consisting of isobutenes and butenes is selected to give a dimer product, which is an isooctene or mixture of isooctenes.   These are subsequently hydrogenated to isooctanes.

The nonselective processes are those in which a mixture of C_2, C_3, and C_4 olefins are charged and the resulting polymer consists of normal and iso-C_4 to C_8 olefins.   The nonselective adaptation is not suitable for the production of high-octane aviation-fuel blending components because of the widely varying mixture of olefins produced.

There are four principal catalytic polymerization processes in use for the production of isooctenes (selective operation).   These use as catalysts the following materials: sulfuric acid, "solid phosphoric acid," copper pyrophosphate, and a water solution of phosphoric acid.   The first three are described in the following section.   The water-phosphoric Acid process is said to be used by the Standard Oil Co. of California.

The Sulphuric Acid Catalytic Process for Polymerization of Butenes.[21]—The Shell companies have developed a catalytic process for the polymerization of the lower olefins, giving a product boiling within the gasoline range and having a relatively high-octane rating. The gasoline produced is composed of unsaturated monoolefins and must be hydrogenated or treated in some manner to reduce the degree of unsaturation when it is to be used as an aviation-fuel base. Such treatment results mainly in loss in blending octane number.

The application of this process to the production of aviation fuel lies in the manufacture of isooctene (diisobutene), which
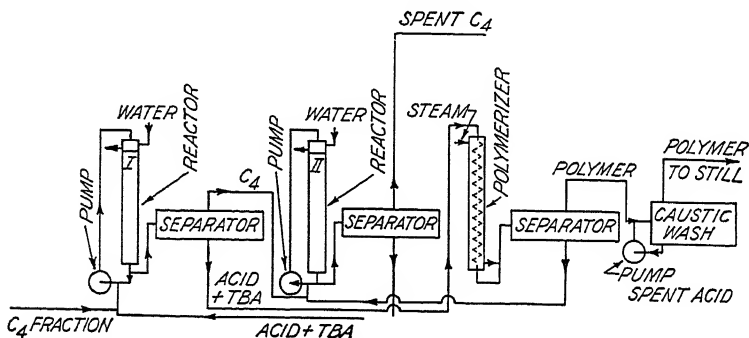
Fig. 7-VI.—Flow diagram of the Cold Acid Polymerization process. (*Courtesy of Refiner Natural Gasoline Mfr.*)

on hydrogenation yields isooctane, an important component of 100 octane aviation fuels. Two processes have been developed using sulfuric acid as a catalyst: the Hot Acid process and the Cold Acid process. The following discussion deals solely with the application of these processes to the manufacture of isooctenes.

THE COLD ACID PROCESS.—This process was the first developed and has been more recently replaced by the Hot Acid process owing mainly to the increased yield obtained from the latter. The flow diagram is shown in Fig. 7-VI. In this method the charge composed of the C_4 fraction from the cracking plant and containing butanes, butenes, and isobutenes is contacted with sulfuric acid of 60 to 70 per cent concentration countercurrently in two stages at 68 to 95°F. Under the conditions outlined, the isobutene is selectively absorbed, leaving the butane and *n*-butenes free. Up to 90 per cent of the isobutenes may be absorbed without absorption of the *n*-butenes.

Three factors are important in the absorption reaction:

1. *Acid strength.* Acid concentration should be below 70 per cent for selective isobutene absorption (minimum concentration 60 per cent).

2. *Acid-to-alcohol ratio.* The higher this ratio the more efficient the absorption. (*tert*-Butyl alcohol is formed from the hydration of the *tert*-butyl sulfate.)

3. *Temperature.* Best between 68 and 104°F.

The acid phase, after it has absorbed a sufficient amount of isobutene, is separated in a separator from the unreacted hydrocarbon layer and passed through a polymerization unit which consists of coils heated to 212°F. The reaction is completed in about a minute and the hydrocarbon layer is separated from the acid, caustic-washed, and distilled. Using 65 per cent sulfuric acid, 75 per cent of the polymer consists of isooctenes or diisobutenes and 25 per cent of the polymer is triisobutene. The advantage of this method is that pure isooctane may be prepared. The yield of octanes is low, averaging 67 per cent of the isobutene charged. Table 10-VI gives a comparison of the Cold and Hot Acid processes.

TABLE 10-VI.—COMPARATIVE EFFICIENCY—COLD AND HOT ACID OPERATION

	Cold acid, 65%, 86–95°F.	Hot acid, 65%, 176°F.	Hot acid, 65%, 194°F.
Feed composition:			
Isobutene, % (wt.)................	18.5	18.5	9.1
n-Butene, % (wt.)................	28.0	28.0	20.6
Butanes, % (wt.).................	53.5	53.5	70.3
Product composition:			
Isobutene, %....................	2.4	0	0
n-Butene, %...................	26.6	15.1	11.4
Butanes, %.....................	53.5	53.5	70.3
Polymer, %.....................	17.5	31.4	18.3
Isobutenes polymerized, %........	87.0	100.0	100.0
n-Butenes polymerized, %.........	5.0	46.0	44.5
Total olefins polymerized, %.......	37.5	67.5	61.5
Polymer composition:			
Sulfur, %.......	0.01	0.03	0.062
Octenes, %.....................	75	88	92
Octane rating of hydrogenated octenes	100	99.2	98.8

THE HOT ACID PROCESS.[21]—The Hot Acid process, derived as a direct outgrowth of the Cold Acid process, utilizes sulfuric acid as a catalyst at temperatures of 140° to 194°F.   This process is superior to the Cold Acid method in that it enables complete utilization of the isobutenes and also causes some of the *n*-butenes to react, thus giving increased yields.   Also, the formation of trimers or the rearrangement to polymers of lower octane number is very much inhibited.   A comparison of the relative efficiencies of the two processes is shown in Table 10-VI.

CHEMISTRY OF PROCESSES.—The reactions for the Cold Acid process may be written as follows: For the absorption step:

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{HCH} & \text{HCH} \\
\text{H} \quad | & \text{H} \quad | \\
\text{HC}=\text{C} \quad + \text{H}_2\text{SO}_4 \cdot & \cdot \text{HC}-\text{C}-\text{HSO}_4 \\
| & \text{H} \quad | \\
\text{HCH} & \text{HCH} \\
\text{H} & \text{H} \\
\text{Isobutene} & \textit{tert-Butyl sulfate}
\end{array}
$$

For the polymerization step:

$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \quad\quad \text{H} \\
\text{HCH} & \text{HCH} & \text{HCH} \quad \text{HCH} \\
\text{H} \quad | & \text{H} \quad | & \text{H} \quad\quad \text{H} \quad\quad \text{H} \\
\text{HC}-\text{C}-\text{HSO}_4 + \text{C}=\text{C} & & \cdot\text{HC}-\dot{\text{C}}-\text{C}-\text{C}=\text{C} + \text{H}_2\text{SO}_4 \\
\text{H} \quad | & \text{H} \quad | & \text{H} \quad | \quad \text{H} \quad\quad \text{H} \\
\text{HCH} & \text{HCH} & \text{HCH} \\
\text{H} & \text{H} & \text{H} \\
\textit{tert-Butyl sulfate} & \text{Isobutene} & \text{2,2,4-Trimethyl pentene-4}
\end{array}
$$

or

$$
\begin{array}{c}
\text{H} \quad\quad \text{H} \\
\text{HCH} \quad \text{HCH} \\
\text{H} \quad | \quad \text{H} \quad | \quad \text{H} \\
\text{HC}-\text{C}-\text{C}=\text{C}-\text{CH} \\
\text{H} \quad | \quad\quad\quad \text{H} \\
\text{HCH} \\
\text{H} \\
\text{2,2,4-Trimethyl pentene-3 (isooctene)}
\end{array}
$$
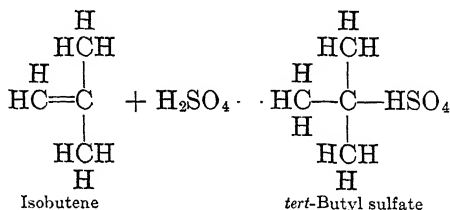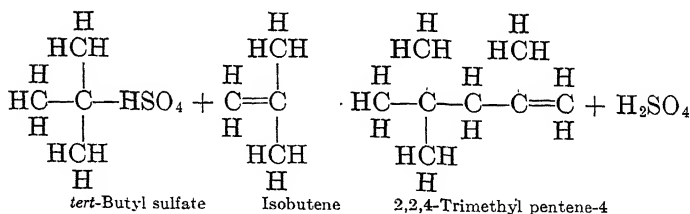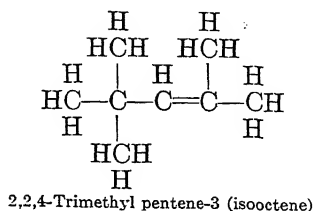
The *tert*-butyl alcohol formation mentioned above is due to the hydration of the *tert*-butyl sulfate thus:

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
\text{HCH} & & \text{HCH} \\
\text{H} \;\; | & & \text{H} \;\; | \\
\text{HC—C·HSO}_4 + \text{HOH} \rightarrow \text{HC—C—OH} + \text{H}_2\text{SO}_4 \\
\text{H} \;\; | & & \text{H} \;\; | \\
\text{HCH} & & \text{HCH} \\
\text{H} & & \text{H}
\end{array}
$$

tert-Butyl sulfate   *tert*-Butyl alcohol
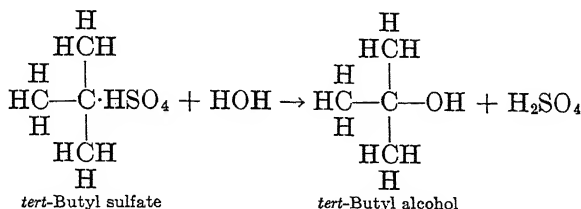
In the Hot Acid process the foregoing reactions take place but in addition some of the *n*-butenes are absorbed by the sulfuric acid forming *sec*-butyl sulfates thus:

$$
\begin{array}{cc}
\text{H H H H} & \text{H H H} \quad\;\; \text{H} \\
\text{HC—C—C=C} + \text{H}_2\text{SO}_4 \cdot & \cdot \text{HC—C—C——CH} \\
\text{H H} \quad\;\;\; \text{H} & \text{\textbackslash} \\
 & \text{H H HSO}_4 \text{ H}
\end{array}
$$

Butene-1   *sec*-Butyl sulfate
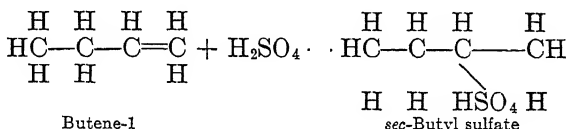
This in turn polymerizes with isobutene or other butenes forming a variety of isooctenes.   For example,

$$
\begin{array}{ccc}
 & \text{H} & \text{H} \quad\;\; \text{H} \\
 & \text{HCH} & \text{HCH HCH} \\
\text{H H H H} \quad\;\;\; \text{H} \;\; | & \text{H} \;\; | \quad\;\;\; | \;\; \text{H H} \\
\text{HC—C—C—CH} + \text{C=C} \quad \cdot \text{HC—C——C—C=C} + \text{H}_2\text{SO}_4 \\
\text{H H} \;\; | \quad\;\;\; \text{H} \quad\;\; \text{H} & \text{H} \;\; | \quad\;\;\; \text{H} \quad\;\;\; \text{H} \\
\text{HSO}_4 \quad\;\;\; \text{HCH} & \text{HCH} \\
 & \text{H} & \text{H}
\end{array}
$$

sec-Butyl sulfate   Isobutene   2,2,3-Trimethyl pentene-4
                                     (isooctene)
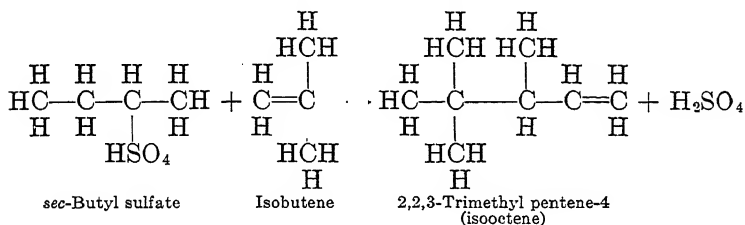
There are several different types of isooctenes produced from these polymerizations.   All the isoolefins, when hydrogenated, have high octane numbers, and the polymer, consisting of a mixture of these, ranges from 98 to 100 octane number after hydrogenation.

The reactions are exothermic and require cooling to keep constant temperatures.

FLOW.—The flow diagram for the Hot Acid process is given in Fig. 8-VI.

The equipment is very similar to that for the Cold Acid process and consists of a jacketed reactor, time tanks, a separator, acid settler, neutralizing tanks, fractionating column, sulfur-removal system, and suitable lines and pumps.

The fresh C_4 feed containing isobutenes, butenes, and butanes enters a line wherein is flowing the recycling emulsion of acid,

polymer, and hydrocarbons.   The mixture is then passed through a jacketed reactor to two time tanks in series.   The effluent from the time tanks is apportioned into recycle emulsion and emulsion to the separator tank.   The acid from the separator is recycled into the system and the remainder of the acid and the hydrocarbon layer is passed to an acid settler.   The acid from this settler is also recycled into the system.   The polymer and unreacted hydrocarbons are neutralized with caustic and fractionated in a tower.   The overhead consists of unreacted butanes-butenes and the residue is a polymer which is desulfurized and sent to storage or to the hydrogenation plant.
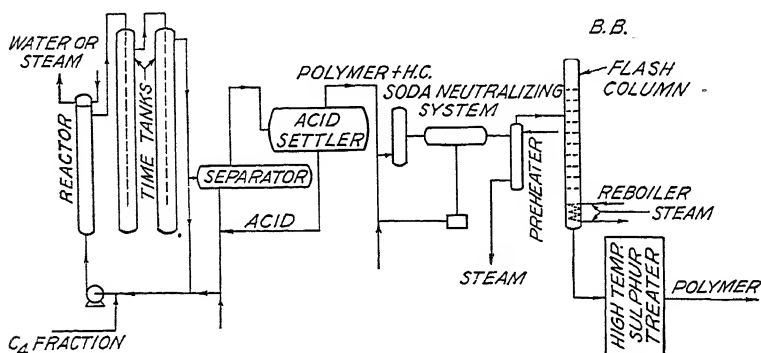
Fig. 8-VI.—Flow diagram of the Hot Acid Polymerization process.   (*Courtesy of Refiner Natural Gasoline Mfr.*)

ELEMENTS OF OPERATION.   *Feed.*—The feed should consist of C_4 hydrocarbons composed of isobutene, butenes, and butanes. The greater the proportion of olefins in the feed, the greater is the efficiency of the process.   Normal feed stocks will range from 30 to 50 per cent olefins, while the ratio of iso- to n-butene in the feed may run from 0.5:1 to 1:1.   However, in the method of flow given above, this ratio actually is very small.

Catalyst.—The sulfuric acid used in this process may range in strength from 63 to 72 per cent and may contain small amounts of organic materials.   There is no loss of acid by reaction and it, therefore, may be used for long periods of time with make-up needed only to replace that lost mechanically.

Temperature and Pressure.—Although the pressure at which the process operates is not specified, it may be deduced that sufficient pressure is maintained in the system to keep the

normally gaseous C_4 hydrocarbons in liquid form at temperatures of around 212°F.

The temperature of operation is closely interrelated with the acid strength used. The range is 167 to 212°F. The weaker acid (63 per cent) is used at the higher temperatures and the stronger acid at the lower temperatures. It is inadvisable to use either the stronger acid or higher temperature since oxidation of the olefins, with the formation of SO_2 and excessive sulfate formation, is more likely under those conditions. Also, at the low acid concentrations and low temperatures, the reaction times are extended and corrosion is more evident. As an average, an acid strength of 67 per cent and a temperature of 189°F. are satisfactory.

Acid-to-hydrocarbon Ratio.—The size of the acid phase influences the reaction in that the larger it is the more rapid the reaction. In practice, the practical acid-to-hydrocarbon ratios range from 2:1 to 1:1.

Contact Time.—The contact time depends upon several factors: the concentration of olefins in the feed stock, the ratio of iso- to *n*-butenes, the temperature, and the strength of the acid. For a given condition an increase in contact time will increase the yield until equal amounts of iso- and *n*-butene are reacted. Beyond this limit the increase in yield is slight. In practice an average contact time of 10 to 15 min. is allowed.

YIELDS.—The yield of polymer depends upon the composition of the feed, the acid-to-hydrocarbon ratio, the acid strength, the temperature of operation, and the contact time. Specific yields under specific operating conditions are found in Table 10-VI.

In general, it is possible to react 90 per cent of the isobutene and 10 per cent of the *n*-butene or completely react the isobutene and an equal quantity (molecular) of the *n*-butenes.

QUALITY OF PRODUCT.—The quality of polymer produced by the Hot Acid process is but slightly less than that produced from the cold process, and the slight loss in quality (on the basis of octane number) is more than compensated for in the increased yield. The reason for the lessened quality is that in the cold process the product is practically pure 2,2,4-trimethyl pentene (100 octane number when hydrogenated), and in the hot process the product when hydrogenated is a mixture of the isooctanes, some of which have octane numbers less than 100.

Table 11-VI gives a comparison between the isooctanes made by the Hot Acid process and technical isooctane.

TABLE 11-VI.—QUALITY OF PRODUCT—HOT ACID
AND TECHNICAL ISOOCTANE

	Hot acid	Technical
Acid heat, °F., Wright.......	24	23
Acid heat, °F., Navy........	3	3
Color, Saybolt..............	30+	30+
Distillation A.S.T.M.:		
Initial, °F..............	208	205
10%, °F................	222	210
30%, °F................	225	210
50%, °F................	226	212
90%, °F................	229	215
Gravity, A.P.I..............	66.5	70.9
Gum, copper dish, mg./100 cc	1	1
Gum, accelerated, mg./100 cc	1	1
Olefins, %.................	1.5	1.8
Sulfur, %..................	0.0001	0.0001
Vapor pressure, Reid, lb.....	2.3	2.1

These data indicate that the quality of the isooctane fraction produced by the Hot Acid process is essentially that of technical isooctane, and that the blending octane values and lead susceptibilities are very similar.

The Solid Phosphoric Acid Catalytic Polymerization Process.[23,24,25,26]—This process, developed and patented by V. N. Ipatieff (of the Universal Oil Products Co.), is capable of producing gasolines of high-octane number as well as diisobutenes or isooctenes which can be converted by hydrogenation into isooctanes. The polymer gasoline, although of high-antiknock rating, is generally unsuitable for use in aviation fuel because of its instability, which is due to the unsaturated hydrocarbons composing the polymer gasoline. Although treatment to reduce the degree of unsaturation would increase the stability, the loss of octane number would be uneconomical under most conditions. Therefore, the most important application of the Phosphoric Acid Catalytic Polymerization process to the manufacture of aviation fuels is in the production of isooctenes from four-carbon-atom olefins. This application is called *selective polymerization*.

CHEMISTRY OF PROCESS.—Under the conditions of nonselective polymerization the reactions are chemical combinations of C_3 and C_4 olefins resulting in C_6 to C_8 monoolefins, the particular product formed depending upon which combinations occur. Under selective polymerization conditions the charging material is, as the term implies, selected and consists of C_4 olefins. These may be n- or isobutenes. The reaction between two molecules results in a dimer (octene) and that between three forms a trimer (dodecene). Theoretically* the combination of two molecules of n-butene results in the formation of n-octene, while the combination of a molecule of n-butene with one of isobutene or that between two isobutene molecules results in one of the isooctenes. These are the type desired for subsequent hydrogenation to isooctanes. Thus, the proportion of iso- to n-butenes influences the final octane number of the polymer due to the type of compound produced.

Sample reactions occurring in the Selective Polymerization process are as follows:
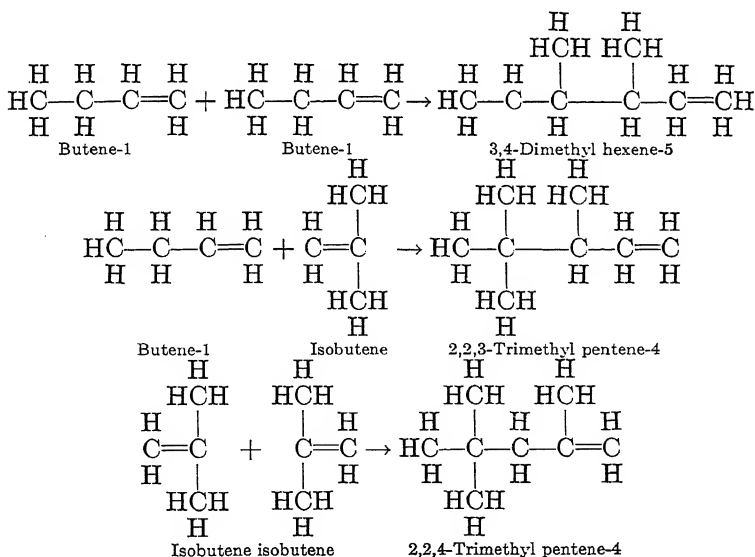
* Tongberg et al.,[22] reporting upon the analysis of a polymer gasoline from nonselective polymerization (charge consisting of C_3 and C_4 olefins), found that 48.1 per cent of the product consisted of C_7 hydrocarbons. These were assumed to be monoolefins although the bromine numbers were too high

or

$$\begin{array}{ccc} & H & H \\ & HCH & HCH \\ H & | & H & | & H \\ HC—C—C{=}C—CH \\ H & | & H \\ & HCH \\ & H \end{array}$$
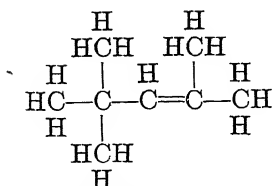
2,2,4-Trimethyl pentene-3

These reactions are mildly exothermic and the amount of heat evolved is proportional to the percentage of olefins in the charge gases.

FLOW.—Figure 9-VI illustrates the flow in the selective Catalytic Polymerization process using solid phosphoric acid as a catalyst. The equipment necessary consists of a caustic-charge gas mixer, caustic settler, surge tank for the butane-butene charge heater, catalyst chambers, debutanizer tower, and a fractionating tower for the separation of the dimers from the trimers (octenes from dodecenes).

The flow is as follows: The butane-butene fraction from the cracked gasoline stabilizer is mixed with caustic to remove sulfur compounds. The caustic wash is settled out in a settling tank and the hydrocarbon mixture is passed to a surge tank, after which it is compressed and liquefied by means of a high-pressure charge pump and passed through a heater. Leaving the heater at a temperature of about 350°F. under a pressure of about 600 lb. per sq. in., the butane-butene mixture is passed through the catalyst reactors. The temperature rise, due to the exothermic nature of the reaction, is controlled by means of a cooling fluid (such as oil) circulated around the reaction tubes. The polymer from the reactors is passed to a debutanizing tower wherein the unreacted paraffin and olefin gases are separated from the polymer. The polymer from the bottom of the tower is fractionated into the octene (or dimer) fraction and dodecene (trimer) fraction in a polymer fractionating tower.

for this class of compounds. It was indicated that the compounds were of the branched, highly reactive type. The properties of one fraction corresponded to those of 3-ethyl pentene-2. This would tend to show that the ordinary reactions are not necessarily followed in catalytic nonselective polymerization. Possibly this is true also of selective polymerization.
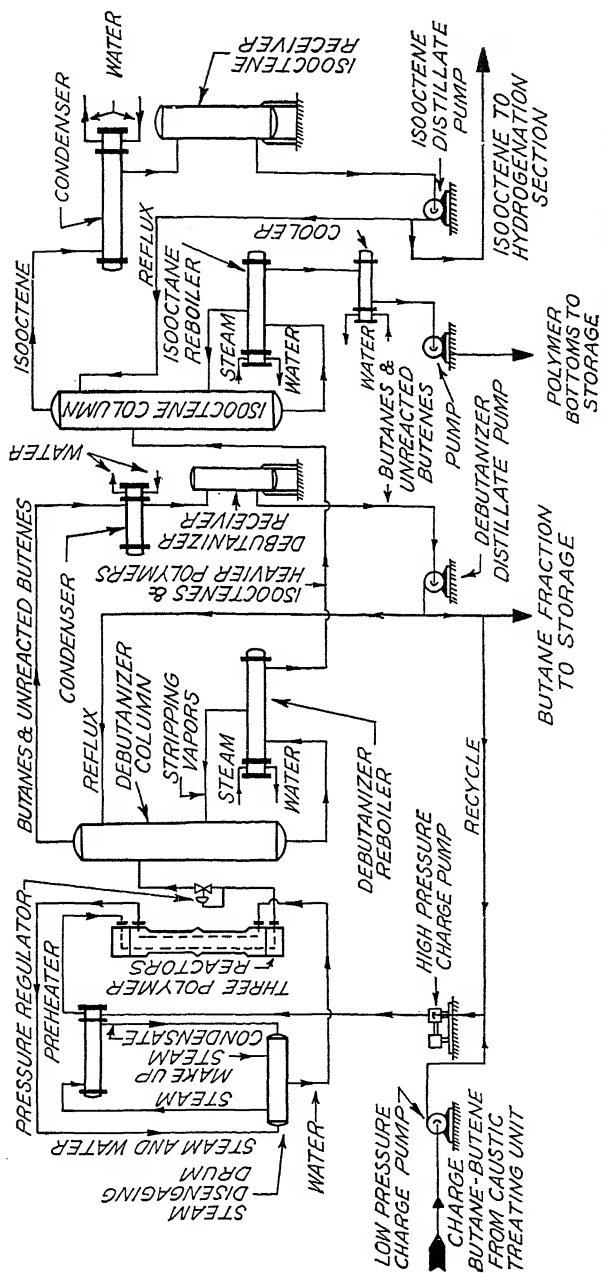
Fig. 9-VI.—Flow diagram of the Solid Phosphoric Acid Polymerization process.   (Courtesy of Refiner Natural Gasoline Mfr.)

ELEMENTS OF OPERATION. *Feed.*—The feed gas for the production of isooctene may consist of the butane-butene fraction of the stabilizer gas from the stabilization of cracked gasoline, dehydrogenated butane and isobutane from any one of several sources, or mixtures of these. The olefinic content of the charge is an important factor in the yield of isooctenes. A typical butane-butene fraction obtained from the stabilizer gas from the stabilization of cracked gasoline has the following composition:

Isobutene, %.. 15.0
n-Butene, %.. 30.0
n- and Isobutanes, %............................. 55.0

This gas is a suitable charging material for selective catalytic polymerization.

Catalytic dehydrogenation of *n*- and isobutanes to the corresponding olefins gives a gas richer in olefins than that shown above.

Sulfur, particularly as hydrogen sulfide, must be removed from the charge gas since it appears in the polymer as mercaptan sulfur. The removal may be effected by any of the accepted processes that are suitable for this purpose.

Catalyst.—The catalyst used in this process is a *solid phosphoric acid* type. The acid is absorbed on clay or some inert material and is used in granular form of definite size and shape. The catalyst is usually packed in tubes around which, in suitable jackets, water, oil, or steam may be circulated to absorb the heat of reaction. The towers are arranged in series, and the number of units depend, on the operating conditions for each particular plant.

After continuous operation for a time the catalyst becomes fouled with a carbonaceous deposit. This deposit lowers the catalytic efficiency and must be removed at regular intervals. The cycle between regenerations varies with conditions of operation. One plant operates each catalyst tower for approximately 60 days before reactivation.

The reactivation is carried out by taking the catalyst tower out of service and burning off the deposit by a controlled oxidation. This is done by passing a stream of combustion gases containing a limited amount of oxygen through the bed. The

temperature of the gases entering the bed is kept at about 600°F. and the maximum temperature below 950°F. The maximum water content of the exit gases is held below 3 per cent.

After the deposit has been burned off, the catalyst is essentially dehydrated and relatively inactive. Its efficiency is restored by steaming at 500°F. for a period of 10 to 16 hr. This effectively rehydrates the phosphoric acid.

Temperature and Pressure.—The temperature and pressure conditions depend upon such variables as the composition of the feed, *i.e.*, the proportion of olefins to paraffins and the ratio of isobutenes to butenes, the time of contact, and the octane number desired in the polymer. These are all interdependent variables and a change in one necessitates a change in the others.

Operating conditions used in one commercial installation are as follows:

Butenes in feed gas, %............................ 45.0
Initial temperature, °F............................ 350
Exit temperature, °F.............................. 500*
Pressure, lb./sq. in............................... 600
Conversion of olefins, %.......................... 67.0
* Estimated.

The temperature rise is due to the heat of reaction and this varies with the proportions of the different olefins in the charge.

YIELDS.—The yield of isooctene depends upon the composition of the feed gas, the conditions of operation such as temperature, pressure, and contact time, and the type of product desired. The higher the octane number desired in the product, the lower

TABLE 12-VI.—ISOOCTANE PLANT OPERATION
Feed:
　n-Butene, %................................. 30.0
　Isobutene, %................................. 15.0
　n- + isobutanes, %.......................... 55.0
Operating conditions:
　Temperature, °F............................. 350–500
　Pressure, lb./sq. in.......................... 600
Conversion:
　Olefins converted, %......................... 67.0
Product:
　Yield, %.............................. .... 30.0
　Composition:
　　Dimer, %...................... .... 85.0
　　Trimer, %...................... . ... 15.0

is the yield obtained. Table 12-VI summarizes the conditions and yield obtained in one commercial installation.

When processing 1,300 bbl. per day of the foregoing butane-butene fraction, 347 bbl. of isooctenes (dimers) and 43 bbl. of trimers are produced.

QUALITY OF PRODUCT.—The isooctenes produced are branched monoolefins ranging from 80 to 85 octane number. Upon hydrogenation the corresponding isooctanes have octane numbers ranging from 90 to 100. Typical of the isooctenes and isooctanes produced by this selective polymerization method are those whose properties are given in Table 13-VI.

TABLE 13-VI.—SELECTIVE CATALYTIC POLYMERIZATION PRODUCTS

	Isooctenes	Isooctanes
Distillation:		
Initial,°F	212	206
10%, °F	213	208
50%, °F	215	210
90%, °F	216	213
E.P., °F	238	244
Octane number (unblended).	84	99
Blending octane number:*		
10%	153	93
20%	138	93
50%	111	97
100%	84	99

* Octane number of blends in the percentage shown with reference fuel A-3 (octane number, 43.6). Motor method (A.S.T.M.) used for octane numbers of 85 and below. A modified method was used for higher octane numbers.

It is interesting to note that the octane rating of the isooctenes is much lower than that of the isooctanes that are produced from them by hydrogenation but the blending octane numbers are very much higher.

COMMERCIAL APPLICATION.—Over 60 catalytic polymerization plants were in operation in the United States in 1942 and more were being built. A greater proportion of these are engaged in selective polymerization.

The Copper Pyrophosphate Catalytic Polymerization Process.[27,28,29,30]—One of the newer catalytic polymerization processes, called the Polyco process, involves the use of copper pyrophosphate as a catalyst for the polymerization of gaseous

olefins to compounds boiling within the gasoline range. The published data are concerned with the conversion of a charge gas containing ethene, propene, and butenes to a polymer gasoline of 82 to 84 octane number and with a blending octane value ranging from 110 to 130. This application is that of nonselective polymerization. However, it is understood that when operated selectively on butane-butene (n- and isobutenes) feed, the product (isooctenes) when hydrogenated has an octane number of 90 and above. Owing to the absence of published data on the use of this process for selective polymerization, the data given here will be limited to the probable flow, conditions of operation, and yields for isooctene manufacture.

The process is licensed by the Polymerization Process Corp. Use of the catalyst is patented under patent U.S. 2189655, issued to R. F. Ruthruff, Feb. 16, 1940.

CHEMISTRY OF PROCESS.—The chemical reactions involved in this process in the selective polymerization of butenes to isooctenes are the same as those in the phosphoric acid selective polymerization. The reactions are exothermic, and apparently the tendency to form dodecenes is somewhat repressed. This gives a product proportionately richer in dimers. For typical reactions see pages 141–142, Chap. VI.

FLOW.—Figure 10-VI illustrates a typical Polyco catalytic polymerization unit. The essential equipment consists of a liquid feed-treating system, feed heater, catalyst cases, product cooler, and a fractionating system for debutanizing and separating the dimers and trimers (applied selective operation).

The feed gases (when the unit is operated for the production of isooctenes), consisting of butenes, isobutenes, n- and isobutanes, are liquefied and passed through a treating system to remove certain impurities, such as sulfur, which impair the efficiency of the catalyst. The feed is then passed through a heater which brings it to the required temperature. From the heater the flow is to the catalyst chambers, usually arranged in series. The effluent from the catalyst chambers is cooled and passed to a fractionation system wherein the unreacted olefins and n- and isobutanes are separated from the polymer, and the polymer is separated into isooctenes and a heavier fraction.

ELEMENTS OF OPERATION. *Feed.*—The feed to the unit, operating selectively for the production of isooctenes, should

consist of a high percentage of C_4 olefins, butene and isobutene, with the remainder being n- and isobutanes. It also should be
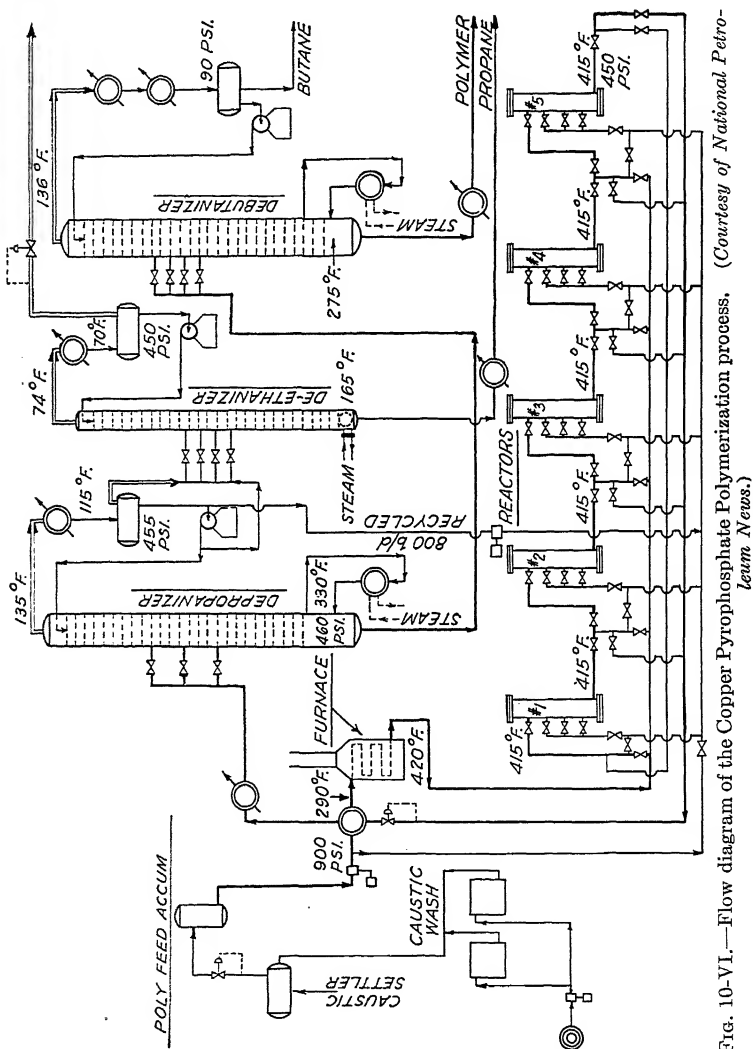
Fig. 10-VI.—Flow diagram of the Copper Pyrophosphate Polymerization process. (Courtesy of National Petroleum News.)

free of impurities such as sulfur, nitrogen compounds, and aromatics that reduce the effectiveness of the catalyst.

Catalyst.—The catalyst is copper pyrophosphate in pellet form. In one installation[27] described in the literature, this material

is arranged in each catalyst tower in four beds supported one above the other on perforated plates. The catalyst is prepared in such a manner that it is rugged and has a relatively long life. It gradually loses efficiency and, after a time, is removed and replaced with fresh catalyst. In one operating unit it is replaced once every 7 or 8 days.

Temperature and Pressure.—Specific operating data for selective operation are not available. For nonselective operation the inlet temperature is around 400 to 425°F. and the initial pressure in the reactors is around 900 lb. per sq. in. The temperature is held relatively constant by circulating a cooling medium, such as gas oil, around the reaction zones. The pressure drops to around 450 lb. per sq. in. at the outlet of the last catalyst chamber.

Yields and Quality of Product.—The yields are dependent upon the composition of the feed (the ratio of olefins to paraffins and the ratio of *n*- to isoolefins), the operating conditions (temperature, pressure, contact time, and condition of catalyst), and the type of product desired. On nonselective operation the yields are said to be around 20 to 30 per cent of the olefin feed as polymer gasoline, with approximately 80 to 85 per cent olefin conversion. For selective operation the yields would probably be comparable.

The octane number of the isooctanes from the hydrogenation of the isooctenes produced by selective operation is reported[31] to be 90+.

Commercial Application.—In 1940 there were two Polyco catalytic polymerization plants in operation and several others under construction.

HYDROGENATION

Hydrogenation may be defined as the chemical addition of hydrogen to a compound. Actually this means the saturation of the hydrocarbon molecule structure with hydrogen, thus reducing double carbon-to-carbon bonds to single bonds. Only hydrocarbon compounds containing double bonds are capable of being hydrogenated. Such hydrocarbons are the olefins, aromatics, and cycloolefins.

From a commercial standpoint the term *hydrogenation* is applied in a broader sense to processes in which both cracking

and hydrogenation occur.   This is called *destructive hydrogenation* and may take place with or without the use of catalysts.   At temperatures of 700 to 1050°F. (temperatures well into the cracking range) and pressures ranging from 300 to 500 lb. per sq. in., oils, tars, and asphalts can be destructively hydrogenated in the presence of hydrogen to produce gasolines of varying yields.   With the use of catalysts, such as molybdenum oxysulfide, molybdenum sulfide, tungsten oxysulfide, and tungsten sulfide, at temperatures from 900 to 1000°F. and relative low pressures of 75 to 300 lb. per sq. in., destructive hydrogenation is also possible.   The rate of hydrogenation is less than when high pressures are used.

Although destructive hydrogenation is of interest, we are primarily interested in the nondestructive hydrogenation processes by which aviation-fuel base materials, such as isooctene, can be converted to isooctane.

Nondestructive hydrogenation processes may not operate at temperatures above 660°F., since at that temperature decomposition reactions are possible.   All the commercial processes are catalytic and use moderate conditions.

Some of the catalysts used are listed as follows:

Hydrogenation catalysts:

Platinum.
Palladium.
Nickel.
Cobalt.
Nickel-cobalt.
Molybdenum sulfide.
Tungsten sulfide.
Molybdenum and tungsten sulfide.

The olefins are more easily hydrogenated than aromatics.   All the foregoing catalysts will enable hydrogenation of olefins under moderate conditions, but only the platinum group will affect hydrogenation of the aromatics.   With the exception of the molybdenum-tungsten sulfide type, the catalysts are easily poisoned by sulfur compounds and are rendered useless in a short time.

The processes used commercially for the hydrogenation of isooctenes to isooctanes use either a low temperature and low pressure, with a nickel catalyst, or high pressure and temperature

in the presence of a sulfur-resistant catalyst, such as molybdenum sulfide.[20] The amount of sulfur contained in the isooctene is usually of the order of 0.0005 per cent, or less, when the nickel catalyst is employed. In the other process, sulfur contents may safely range much higher. This initial sulfur content is removed during hydrogenation and will not appear in the finished isooctane product.

Catalytic Hydrogenation (Low Pressure)[32] Shell Process.— The hydrogenation of isooctenes to isooctanes is an important phase in manufacturing one of the elements of aviation fuel. A catalytic process operating in the vapor phase using nickel as a catalyst was developed by the research staffs of the Shell Development Co. and the Shell Chemical Co.

CHEMISTRY OF PROCESS.—The chemistry of the hydrogenation of isooctene to isooctane is shown by the following reaction:

$$
\begin{array}{ll}
\begin{array}{ccc}
& \text{H} \quad\;\; \text{H} & \\
& \text{HCH} \;\; \text{HCH} & \\
\text{H} & \text{H} \qquad \text{H} & \\
\text{HC}\!-\!\overset{\cdot}{\text{C}}\!-\!\text{C}\!=\!\overset{\cdot}{\text{C}}\!-\!\text{CH} & + \text{H}_2 \\
\text{H} & \qquad\;\; \text{H} & \\
& \text{H}\overset{\cdot}{\text{C}}\text{H} & \\
& \text{H} & \\
& \text{Isooctene} \qquad \text{Hydrogen} &
\end{array}
&
\begin{array}{ccc}
\text{H} \quad\;\; \text{H} & \\
\text{HCH} \;\; \text{HCH} & \\
\text{H} \;|\; \text{H} \;|\; \text{H} & \\
\text{HC}\!-\!\text{C}\!-\!\text{C}\!-\!\text{C}\!-\!\text{CH} & \\
\text{H} \;|\; \text{H} \;\; \text{H} \;\; \text{H} & \\
\text{HCH} & \\
\text{H} & \\
\text{Isooctane} &
\end{array}
\end{array}
$$
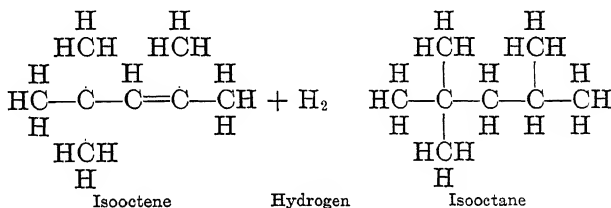
This reaction shows the hydrogenation of 2,2,4-trimethyl pentene-3 to 2,2,4-trimethyl pentane. Other isooctenes are hydrogenated in the same manner with the complete saturation of the double bond. The reaction is highly exothermic.

FLOW.—Figures 11-VI, 12-VI, and 13-VI illustrate the types of flow utilized in this process.

The principal equipment necessary for the type of flow shown in Fig. 11-VI consists of an octene vaporizer, a hydrogen heater, a converter or catalyst chamber, octane condenser, octane receiver, and a heating and cooling system for the fluid that is circulated through the converters to maintain temperature control. This system consists of a furnace, a cooler, and suitable pumps and lines so that the temperature-control fluid coming from the converters may be either heated or cooled as necessary.

In the single-stage flow shown in Fig. 11-VI, the liquid octene feed is vaporized and mixed with hydrogen, which has been heated to the desired temperature, and the vapor mixture is

passed through a catalyst converter (or several in series). The product from the converter is condensed and taken to the octane receiver in which the unreacted hydrogen is removed, and part of it is recycled to the line in which the octene vapor-hydrogen mixture is passing to the converter.
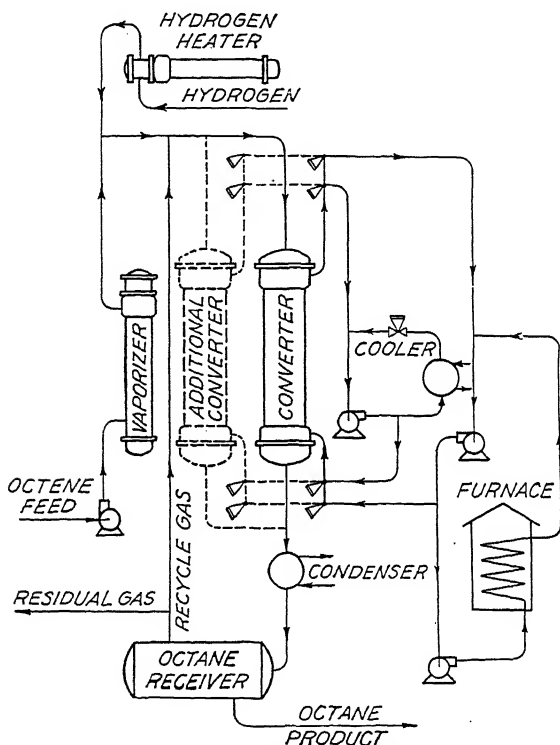
Fig. 11-VI.—Flow diagram of the single stage Catalytic Hydrogenation process (Shell). (*Courtesy of Refiner Natural Gasoline Mfr.*)

The type of flow shown in Fig. 12-VI uses the same equipment as the regular single-stage flow with the addition of more catalyst chambers. These are called *catalyst guard tubes* and, in practice, are the converters that have become inefficient for hydrogenation catalysis but still have the ability to remove sulfur compounds. The flow differs from the simple single-stage flow in that the octene vapors and part of the hydrogen are passed through the guard tubes first for sulfur removal, and then, with the addition of more hydrogen to the mixture from the guard tubes, the

desulfurized octene vapors and hydrogen are passed through the converter where hydrogenation takes place.

In the two-stage countercurrent system shown in Fig. 13-VI, the equipment needed is in duplicate of that necessary for the single stage, with the addition of suitable heat exchangers to prevent excessive loss of heat.   The flow is the same as if there
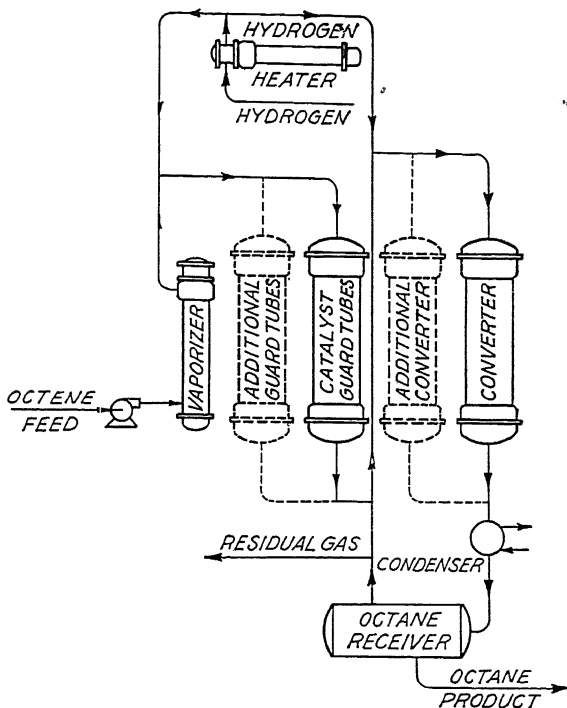
FIG. 12-VI.—Flow diagram of the single-stage Catalytic Hydrogenation process using catalyst guard tubes (Shell).   (*Courtesy of Refiner Natural Gasoline Mfr.*)

were two single-stage systems in series, with the exception that fresh hydrogen is added to the second stage and the recycle gas from both stages constitutes the hydrogen feed to the first stage.   Thus, countercurrent flow of the hydrogen is effectively established.

ELEMENTS OF OPERATION.   *Feed.*—The feed consists of the isooctene mixture derived from polymerization processes.   Pure compounds such as diisobutene and triisobutene are also hydrogenated effectively by this process.   The olefin charge should

contain a minimum amount of sulfur compounds, since the catalyst efficiency is greatly reduced by such impurities. Where catalyst guard tubes are used, the maximum allowable sulfur content may be higher than when they are not used. A sulfur content of 0.0005 per cent or less causes only slow catalyst deactivation.
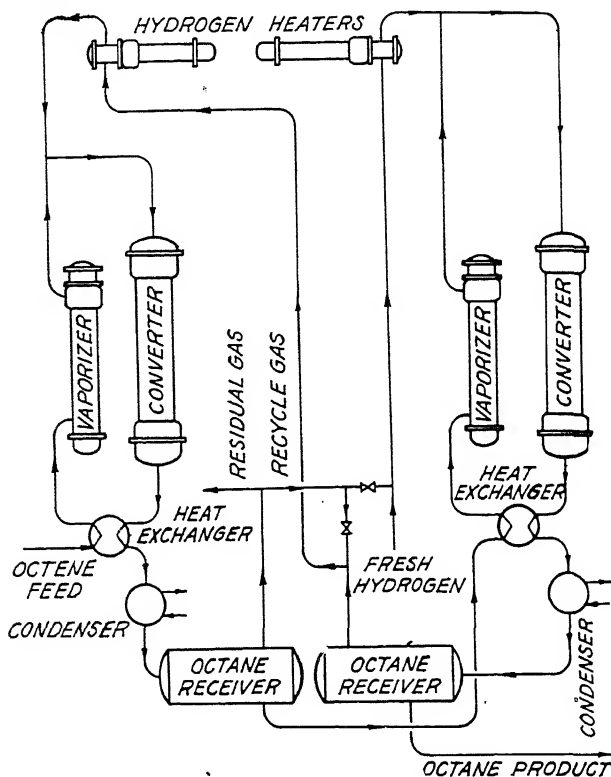
FIG. 13-VI.—Flow diagram of the two-stage Catalytic Hydrogenation process (Shell). (*Courtesy of Refiner Natural Gasoline Mfr.*)

The hydrogen may contain impurities as long as they do not interfere with the Hydrogenation process by dilution of the reactants or poisoning of the catalyst. Pure hydrogen, mixtures of hydrogen and nitrogen, etc., are satisfactory. The hydrogen may be obtained from such sources as pyrolysis of natural gas and decomposition of ammonia. Another source of hydrogen, suitable for the Catalytic Hydrogenation process, is claimed for

the Catalytic Dehydrogenation process (see page 120, Chap. VI). Concentrations of hydrogen in the feed gas of 75 to 95 per cent (and above) have been used successfully. Hydrogen concentration 10 to 15 per cent in excess of the theoretical is needed in the single-stage process to reduce the reaction time. Recycling 50 to 80 per cent of the residual gas containing around 80 mol per cent of hydrogen effects a saving of 5 to 10 per cent in the original hydrogen charged. Two-stage countercurrent operation also saves hydrogen. In one case described,[32] the mol ratio (in the converters) of hydrogen to octenes ranged from 1.12 to 1.37 (the latter ratio is the result of recycle gas plus fresh hydrogen added while the former was the result of fresh hydrogen charge alone).

Catalyst.—The catalyst consists of activated nickel based on porcelain. It is prepared by impregnating porcelain with nickel nitrate (hydrated), decomposing it to the oxide with air, and reducing the oxide to finely divided metallic nickel with hydrogen. It is necessary to keep the prepared catalyst in a hydrogen atmosphere since air rapidly oxidizes it.

Carbon monoxide, oxygen, and sulfur all react with the catalyst and deactivate it. The oxide may be reduced in place, but the sulfide formation results in permanent loss in activity.

Reactivation, in the case of sulfur poisoning and carbon deposition, is carried out by purging the catalyst bed of hydrogen (by steam) and then oxidizing with air for 4 to 12 hr. The oxidized catalyst is then reduced with hydrogen. Such reactivation when made from two to four times in place increases the catalyst life at least 150 per cent. The activity is lower after each reactivation but is still sufficiently great to enable efficient hydrogenation. The catalyst is finally removed and reprepared after its efficiency has dropped to an uneconomical point. This is determined by the through-put capacity for a given volume of catalyst.

In commercial installations the catalyst is contained in 3-in.-diameter vertical tubes, bundled in a heat exchanger type of chamber. Cooling or heating fluid circulates around the outside of the tubes to maintain temperature control.

In using guard catalyst tubes, usually one volume of guard catalyst is sufficient for two volumes of catalyst.

Temperature—Pressure.—The temperature in the reactors is maintained at 356 to 374°F. The pressure used is 15 to 60 lb.

gauge. Below 350°F. the reaction rates are low. Above 375°F. there is a tendency toward decomposition of the olefins, which causes carbon deposition on the catalyst and increases hydrogen consumption. Higher pressures tend to increase the rate of reaction and cause overheating.

The reaction is exothermic, and the heat of reaction is reported to be 450 B.t.u. per lb. Provision is made to remove the excess heat by the method described above.

YIELDS AND QUALITY OF PRODUCT.—The yield of isooctane, in one plant described, averaged 103.0 per cent by volume of the octene feed (theoretical, 105.5 per cent by volume of diisobutene charged). Conversion of 99 per cent is claimed. Eighty-six to 95 per cent of the hydrogen has been utilized, producing a 99 per cent saturated octane fraction. With three reactivations and using catalyst guard tubes, 1,000 gal. of octanes can be produced per pound of catalyst.

TABLE 14-VI.—PROPERTIES OF OCTANES

Octane from:	Octene fraction	Technical isooctene
Acid heat, Wright, °F	26	23
Acid heat, Navy, °F	7	3
Color, Saybolt	30+	
Distillation, A.S.T.M.:		
Initial, °F	196	205
10%, °F	221	210
30%, °F	225	210
50%, °F	227	212
80%, °F	230	214
90%, °F	231	215
E.P., °F	236	235
Gravity, A.P.I	66.3	70.9
Gum, copper dish, mg./100 cc	1	1
Gum, accelerated, mg./100 cc	1	1
Octane number, A.S.T.M	98.2	99.7
Sulfur, %	0.0001	0.001
Unsaturation, %	1.1	1.8
Vapor pressure, Reid, lb	2.6	2.1

Table 14-VI lists the quality of octanes prepared from this hydrogenation process compared to those of technical isooctane.
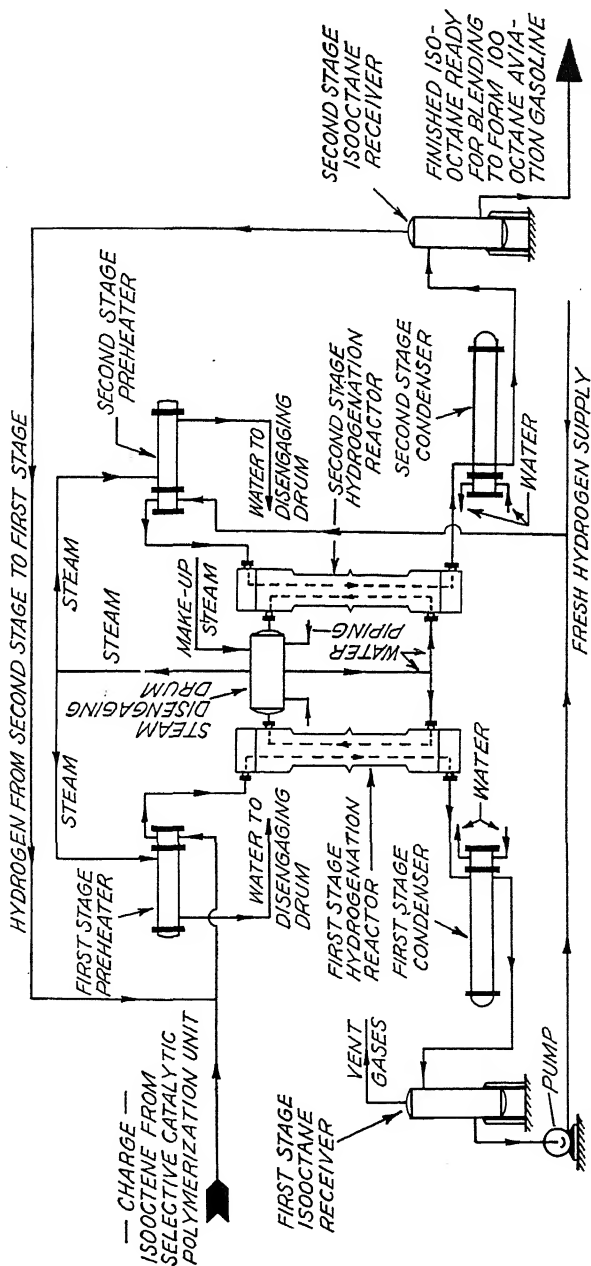
Fig. 14-VI.—Flow diagram of the U.O.P. Catalytic Hydrogenation process.   (Courtesy of Refiner Natural Gasoline Mfr.)

COMMERCIAL APPLICATION.—There are several low-pressure hydrogenation plants in operation whose purpose is to hydrogenate the isooctenes formed from selective polymerization.

Catalytic Hydrogenation,[33,19,34] **U.O.P. Process.**—The U.O.P. Hydrogenation process is similar to that developed by the Shell companies. Its principal use is in conjunction with the Catalytic Phosphoric Acid Polymerization process to hydrogenate the octene product from the polymerization step.

The flow diagram shown in Fig. 14-VI illustrates a two-stage, countercurrent process that utilizes 95 per cent of the hydrogen. The octene mixture entering the system is mixed with residual hydrogen from the second stage, heated, and passed through the first-stage reactor. The partly hydrogenated octenes are condensed and the gas vented. The octene-octanes are then mixed with fresh hydrogen and passed to a second reactor. The mixture is cooled, the octanes condensed and stored, and the residual gas added to the incoming octene mixture. Water is maintained around the tubes in the reactors to absorb the exothermic heat of reaction, which is converted to steam. With some outside steam added, this is used to heat the hydrogen octene and hydrogen-octene-octane mixture.

The catalyst used in this process is activated nickel, the same as that used in the Shell process. The conditions of operation are temperature, 300 to 325°F. and pressure, 75 lb. per sq. in. The product averages 95 octane number.

Catalytic Hydrogenation (High Pressure).[35]—A high-pressure moderate-temperature hydrogenation process is in operation, which, although developed primarily for the hydrogenation of naphthas, will suitably hydrogenate octene mixtures to octanes. The catalyst used has the advantage of being sulfur-resistant, thus allowing octene mixtures containing relatively large amounts of sulfur to be hydrogenated without previous sulfur-removal treatment. This plant is operated by the Standard Oil Co. of Louisiana.

FLOW.—The flow diagram for this process is shown in Fig. 15-VI. The flow is as follows: The isooctene mixture and hydrogen feed are compressed separately to around 3,000 lb. per sq. in., passed through a heat exchanger heated by the reaction products, and then brought to temperature by heating in a fired coil. The

heated-gas and isooctene mixture is then passed through the catalyst chamber where hydrogenation takes place. The liquid isooctanes are cooled, the pressure is released, and the unused hydrogen separated. The isooctanes are stored for use.

ELEMENTS OF OPERATION. *Feed.*—The feed for the production of isooctanes consists of an isooctene mixture and hydrogen. Since the catalyst used is not susceptible to sulfur poisoning, the
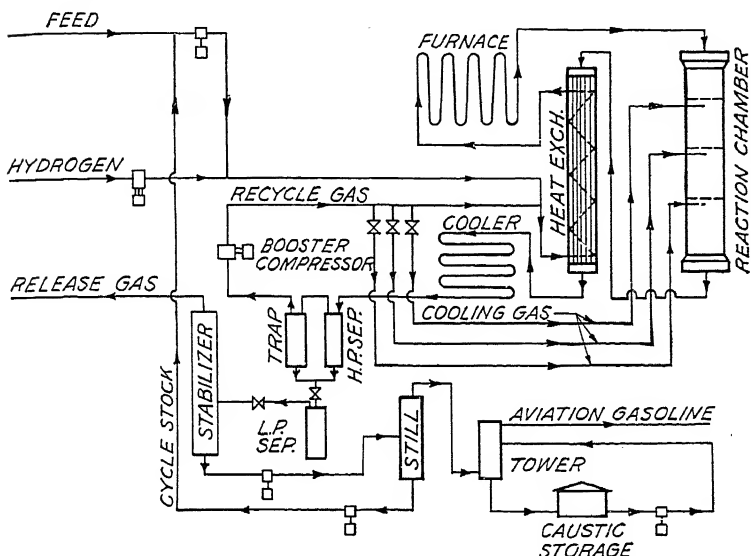
FIG. 15-VI.—Flow diagram of the High-pressure Catalytic Hydrogenation process. (*Courtesy of Oil Gas J.*)

charge may contain higher quantities of sulfur than when nickel is used.

Catalyst.—The catalyst used is reported[31] to be of the sulfur-resistant molybdenum type.

Temperature and Pressure.—The pressure of the operation is maintained around 3,000 lb. per sq. in.

QUALITY OF PRODUCT.—It may be assumed that yields in this process are as high as those obtained in other forms of hydrogenation. Table 15-VI lists the properties of the hydrogenated dimer and codimer produced from this process.

COMMERCIAL APPLICATION.—There were five plants using the High-pressure Hydrogenation process in 1940.

TABLE 15-VI.—PROPERTIES OF OCTANE MIXTURES

	Hydrogenated dimer*	Hydrogenated codimer†
Acid heat, °F...............	2	1
Bromine number, g./100g....	3	1
Distillation, A.S.T.M.:		
Initial, °F.........	178	161
10%, °F..................	207	213
50%, °F..................	212	224
90%, °F..................	216	231
E.P., °F..................	249	243
Gravity, A.P.I..............	70.9	67.6
Gum, copper dish, mg./100cc.	0.9	0.5
Octane number, A.S.T.M.....	99	96.5
Sulfur, %.................	0.004	0.006
Vapor pressure, Reid, lb.....	2.8	2.8

* Dimer, diisobutene.
† Codimer, polymers of iso- and n-butenes.

ALKYLATION

The term *alkylation* formerly was defined as the substitution of an aliphatic hydrocarbon radical for a hydrogen atom in a cyclic compound. Thus, the substitution of a methyl group for a hydrogen in benzene, forming toluene, was termed *alkylation*. Recently, general usage has broadened the definition of alkylation to the substitution of an alkyl (aliphatic) group for the hydrogen atom on any organic chemical compound. The substitution of isobutane for a hydrogen atom on the butane molecule, forming isooctane, is called *alkylation*.

This type of reaction is of particular interest to petroleum technologists since it can be used to form compounds of high-antiknock value from hydrocarbons that, in themselves, have relatively low economic value. Through alkylation, 2-, 3-, and 4-carbon gases can be transformed into high-antiknock fuels.

There are two principal types of alkylation processes which are in use at the present time: catalytic alkylation and thermal alkylation.

Catalytic Alkylation.—Catalytic alkylation effects the formation of high-antiknock compounds from olefin and paraffin hydrocarbons by the use of catalysts at low temperatures and pressures. This type of alkylation has been the subject of much research

and much of this work has been reported in the literature. There have been many catalysts investigated and reported upon. Table 16-VI lists some of the catalysts described.

TABLE 16-VI.—CATALYTIC ALKYLATION

Catalyst	Temperature-pressure	Charge material	Ref.*
$AlCl_3$	Atmospheric and above	$C_6H_{14} + C_2H_4$, $iC_4H_{10} + C_2H_4$	3
$AlCl_3$	Below 32°F.	$iC_4 + iC_4$	16
$AlCl_3$	....	Olefin gas, st.-run gasoline	2
$AlBr_3$	....	Olefin gas, st.-run gasoline	2
$AlCl_3 + HCl$	−58° to +167°F.	$C_3, C_4, iC_4 + C_3{}^=, C_4{}^=, iC_4{}^=$	9, 11, 13, 14
$NaCl·AlCl_3$	400°F. 1,000 lb./sq. in.	$iC_4{}^= + iC_4{}^=, C_4{}^=, C_3{}^=, C_2{}^=$	30
$LiCl·AlCl_3$	400°F. 1,000 lb./sq. in.	$iC_4 + iC_4{}^=, C_4{}^=, C_3{}^=, C_2{}^=$	30
$SbCl_5$	....	Olefin gas, st.-run gasoline	2
$BF_3 + HF$	−58 to +50°F.	iC_4 + gaseous olefins	15
$BF_3 + Ni + HF$	−58 to +50°F.	Gaseous paraffins + olefins	12, 27
$CuS_2O_7 + H_2SO_4$	....	$iC_4 + C_4{}^=$	23
Chlorosulfonic acid	0°F. to m.p. of acid	iC_4 + gaseous olefins	24
HF	....	$iC_4 + C_4{}^=$	26
Oxides of Vth group	0 to 120°F., 0 to 1,200 lb./sq. in.	....	29
H_3PO_4	10 to 400°F., 1 to 41 atm.	$iC_4{}^=, iC_4+C_3{}^=, C_4, C_4{}^=$	4, 5, 6, 8, 28
$H_3PO_4 + H_2SO_4::3:2$	150 to 300°F.	Gaseous olefins	20
H_2SO_4	....	Cracking gases + st.-run gasoline	1
H_2SO_4 90–100 %	−14 to +86°F. 0–80 lb./sq. in.	$iC_4, iC_3 + C_4{}^=, iC_4{}^=$	6, 7
H_2SO_4	60 to 176°F., v.p. of iC_4	iC_4 + olefins ($C_3{}^=$)	17, 22
$H_2SO_4 + Cd_3(PO_4)_2$	....	$iC_4 + C_4{}^=$	19
$H_2SO_4 + CuSO_4$	−10 to +30°F. (liquid phase)	$iC_4 + C_2{}^=$	18
$H_2SO_4 + HgSO_4$	−10 to +30°F. (liquid phase)	$iC_4 + C_2{}^=$	18
$TaCl_5$ or $TaBr_5$	....	Olefin gas + st.-run gasoline	2
$SnCl_4$	....	Olefin gas + st.-run gasoline	2
$TiO_2 + SiO_2$	350 to 400°F.	$iC_6 + C_2{}^=$	25
WCl_6	....	Olefin gas + st.-run gasoline	2
$V_2O_3 + SiO_2$	350 to 400°F.	$iC_6 + C_2{}^=$	25
$Zn + HCl$	−50 to +20°F.	$C_4 + C_4{}^=$	21
$ZrCl_4 + HCl$	68 to 167°F.	$C_3, iC_4 + C_3{}^=, C_4{}^=$	10

* See reference list immediately following this table.

References for Table 16-VI

1. IPATIEFF (Universal Oil Products Co.), U.S. 2001906.
2. IPATIEFF and GROSSE (Universal Oil Products Co.), U.S. 2057432.
3. IPATIEFF *et al.; J. Am. Chem. Soc.*, **58**, 913 (1936).
4. Universal Oil Products Co., Brit. 477128.
5. Universal Oil Products Co., Fr. 818930.
6. DUNSTAN, Brit. 479345.
7. N.V. de Bataafsche Petroleum Maatschappij, Fr. 824329.
8. LYMAN (Standard Oil, Calif.), U.S. 2135823.
9. Universal Oil Products Co., Brit. 496273.
10. Universal Oil Products Co., Brit. 498127.
11. Universal Oil Products Co., Brit. 497792.
12. Universal Oil Products Co., Brit. 486355.
13. Universal Oil Products Co., Fr. 823592.
14. Universal Oil Products Co., Fr. 823593.
15. Universal Oil Products, Fr. 823594.
16. IPATIEFF (Universal Oil Products Co.), U.S. 2170306.
17. Texaco Development Corp., Brit. 515367.
18. Anglo-Iranian Oil Co., Brit. 526165.
19. BRADLEY (Union Oil Co. Calif.), U.S. 2201823.
20. LAUGHLIN (Standard Oil Development Co.), U.S. 2199180.
21. MORRELL (Universal Oil Products Co.), U.S. 2202115.
22. Standard Oil Development Co., Brit. 527055.
23. BLOUNT (Union Oil Co., Calif.), U.S. 2225544.
24. BRADLEY (Union Oil Co., Calif.), U.S. 2255610.
25. CHAPPELL, U.S. 2266848.
26. GROSSE (Universal Oil Products Co.), U.S. 2267730.
27. IPATIEFF (Universal Oil Products Co.), U.S. 2217019.
28. PINKERTON (Sinclair Refining Co.), U.S. 2233144.
29. Standard Oil Development Co., Brit. 535064.
30. *Ind. Eng. Chem.*, **32**, 328 (1940).

From Table 16-VI it can be seen that most of the catalytic alkylation processes studied are based upon the utilization of the isoparaffins, isobutane, and isopentane. For the purposes of aviation-fuel manufacture, isopentane is valuable in itself since it has a high volatility and a high-octane number, and as a result, isobutane is, in most cases, the material used. For our present and projected aviation-fuel program the natural supply of isobutane is not sufficient, and isomerization is resorted to in order to convert abundant supplies of butane (which is unreacted in the present commercial catalytic alkylation processes) to isobutane (see Catalytic Isomerization, page 127).

The catalytic alkylation processes in use at present are selective in that they react the isoparaffins easily. Isobutene, normal butene, and propene are reacted easily while ethene is reacted with difficulty. It is interesting to note that the relative reactivity in this type of alkylation is the reverse of that found in the case of thermal alkylation (see page 173).

The olefins necessary for catalytic alkylation are usually available in sufficient quantities from cracking processes. In some instances, it may be necessary to change operating conditions of existing cracking facilities to produce the type and quantity of olefins desired.

The two principal processes of commercial importance in the field of catalytic alkylation are the Sulfuric Acid process and the Hydrofluoric Acid process. These are discussed in detail in the following pages.

Sulfuric Acid Alkylation Process—"Cold Acid" Process.[30,36,37] An important commercial process for the production of isooctane is the Sulfuric Acid Alkylation process, commonly called the *Cold Acid* process. This process was developed to its present state by the combined efforts of the staffs of the Anglo-Iranian Oil Co., Ltd., Humble Oil and Refining Co., Shell Development Co., Standard Oil Development Co., and the Texas Corp. Originally, independent research by all these companies resulted in the development of the same process although individually there were differences in details of operation.

CHEMISTRY OF PROCESS.—Although there is not a definite agreement on the theory of the reactions in sulfuric acid alkylation, it is generally believed that the reaction takes place in two steps: the absorption step and the coupling step.

In the absorption step the olefins are absorbed by the sulfuric acid forming alkyl esters. This is shown in the following equations:

$$
\underset{\text{Butene-1}}{\overset{\displaystyle \mathrm{H\ \ H\ \ H\ \ H}}{\underset{\displaystyle \mathrm{H\ \ H\ \ \ \ \ H}}{\mathrm{HC\!-\!C\!-\!C\!=\!C}}}} + \mathrm{H\cdot HSO_4} \rightarrow \underset{\text{Butyl ester of } H_2SO_4}{\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H\ \ H\ \ H}}{\overset{\displaystyle \mathrm{HCH}}{\overset{\displaystyle \mathrm{H\ \ H\ \ |}}{\mathrm{HC\!-\!C\!-\!C\!-\!HSO_4}}}}}}
$$
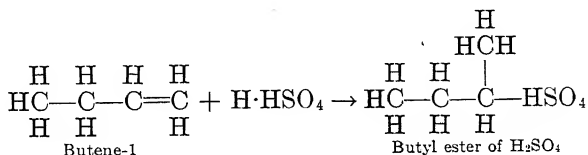
In the coupling step, the alkyl esters condense with the isoparaffins, splitting off sulfuric acid, thus

```
      H                  H
     HCH                HCH
 H  H  |            H   |   H
HC—C—C—HSO₄  +  HC—CH ·
 H  H  H            H   |   H
                       HCH
                        H
   Butyl ester         Isobutane
```

```
                         H     H
                        HCH   HCH
          H   H                      H
         HC—C—┘         Ċ—CH  +  H₂SO₄
          H   H   H     |    H
                       HCH
                        H
              2,2,3-Trimethyl-pentane
                    (isooctane)
```
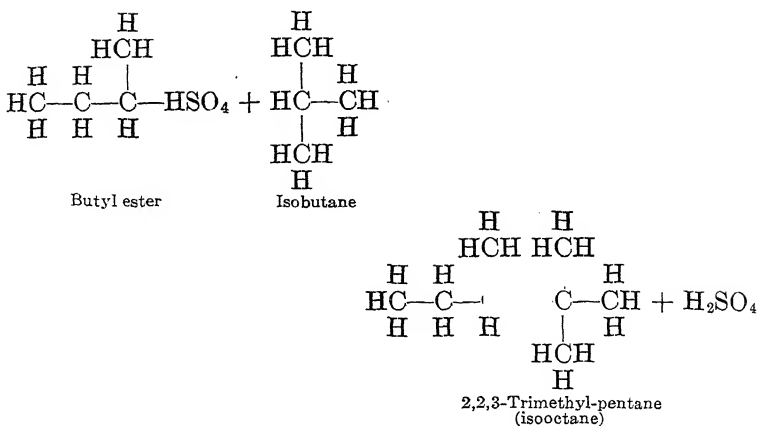
The reactions are exothermic and require external refrigeration for temperature control.
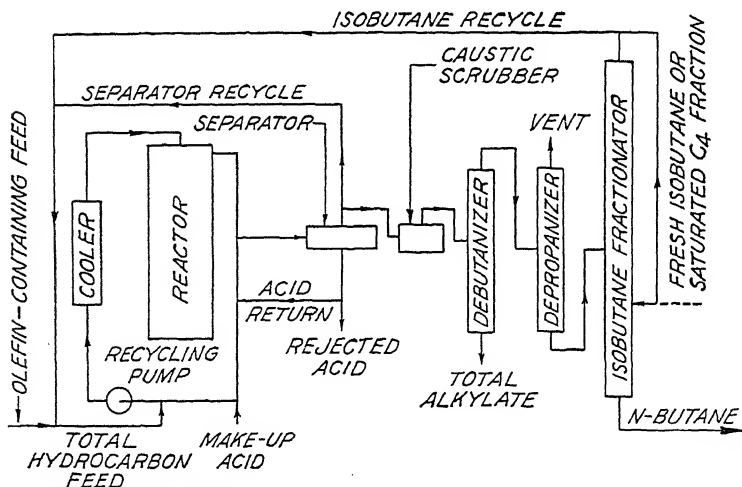
FIG. 16-VI.—Flow diagram of the Sulfuric Acid Alkylation process. (*Courtesy of Refiner Natural Gasoline Mfr.*)

FLOW.—A simplified flow sheet of the process is shown in Fig. 16-VI.   The principal elements of the process are the chilling chamber, reactor, acid-hydrocarbon separator, caustic scrubber, debutanizing and depropanizing towers, and the isobutane fractionator.

The olefinic feed charge, containing relatively high olefinic concentration comprising olefins of the order C₃ to C₈, is combined

with the isobutane feed and mixed with 90 to 100 per cent H_2SO_4. The acid-hydrocarbon mixture is pumped through a refrigerated chiller and then into a reactor. The effluent from the reactor flows to a gravity separator wherein the acid separates from the hydrocarbon. The acid, part of which is withdrawn, is mixed with fresh acid and recycled into the system. The hydrocarbon mixture, consisting of alkylate, propane, butane, and isobutane, is passed through a caustic scrubber which removes any traces of acid that would corrode the fractionators. The scrubbed hydrocarbon then enters a debutanizing tower where the C_3, C_4, and iso-C_4 constituents are removed overhead and the alkylate is removed from the bottom of the tower.

The overhead is conducted to a depropanizing tower in which the propane is removed from the top and C_4 and iso-C_4 from the bottom. The butanes are then separated by fractionation and the iso-C_4 added to the iso-C_4 charge to the system. The butane is stored.

ELEMENTS OF OPERATION. *Feed Stocks.*—The olefin feed to the system may consist of mixtures of hydrocarbons containing a relatively high percentage of olefins from C_3 to C_8. Lower olefins (less than C_3) tend to increase acid consumption, as do the diolefins, while higher olefins (higher than C_8) tend to form compounds of too high boiling range. If the isoparaffin-olefin ratio is kept constant, the concentration of olefin in the total feed is of secondary importance. At a 5:1 isoparaffin-olefin ratio, the recommended concentration of olefin is 8 to 14 per cent of the total hydrocarbon feed. The presence of relatively large amounts of n-paraffins requires an increase in the isoparaffin-olefin ratio. The isoparaffin feed should consist essentially of a hydrocarbon mixture containing a high percentage of isobutane and isopentane (for the production of high-octane alkylate in the desired boiling range for aviation fuel). Normal isobutane stocks from refinery gases usually contain sulfur compounds, nitrogen compounds, aromatics, etc., which cause an increased consumption of acid. However, in some cases the cost to remove such materials would be greater than the saving effected from reduced acid consumption. Isopentane and isohexane are usually of too great a value in themselves as high-octane blending agents to be used in the isoparaffin charge for alkylation.

Isoparaffin-olefin Ratio.—It has been found[36] that the greater the isoparaffin-olefin ratio the higher the total yield, the greater the percentage of aviation fraction, the higher the octane number of the product and the lower the acid consumption. The greatest effective increase takes place between the ratios of 2:1 to 5:1. Therefore, the ratio of 5:1 is usually considered the minimum. In some cases[37] the isoparaffin-olefin ratio may range from 4:1 to 15:1, with an average of 7:1. Thus, the limit of operation of this process depends greatly upon the available supply of isobutane (or isoparaffin). An increase in the ratio is effected by the recycling of the isobutane which has passed through the system into the fresh isobutane charge. This increase also may be obtained by operating several stages in series, splitting the olefin feed between the stages.

Contact Time.—The contact time allowed for low-temperature H_2SO_4 alkylation ranges from 5 to 40 min. (The contact time is usually taken as the ratio of the volume of the hydrocarbon phase in the reaction zone to the volume of the total hydrocarbon feed, per unit of time.) The optimum contact time varies with type of feed stock, concentration of acid, strength of acid, etc.

Acid Strength and Consumption.—Lower strength acids[36] are more effective at higher temperatures, while the stronger acids, 98 to 100 per cent, are more effective at lower temperatures (below 70°F.). Make-up acid strength usually runs 96 to 100 per cent, while the acid in the reactor runs 88 to 90 per cent. A minimum of 90 per cent acid is recommended, and regular "black" plant acid may be used.

Acid consumption may vary widely with the character of feed stocks, temperature, etc. Usually the higher the temperature, the greater the acid consumption. -Dienes, lower olefins, sulfur and nitrogen compounds also increase acid consumption. The normal acid consumption given by one writer[37] is 0.8 to 1.0 lb. of acid per gallon of alkylate produced or 1 gal. of acid per 15 gal. of alkylate.

Acid-hydrocarbon Ratio.—The volume ratio of acid to hydrocarbon in the reaction zone is important. In one case[36] it is recommended that it be kept to the limits of 1:1 to 2:1, with 1:1 in most cases being satisfactory. Another author states that the effect of this ratio is critical and should be kept from 0.7:1 to 1:1; otherwise tight emulsions may be formed. This

difference probably is due to the type of charging stock used.

Temperature.—The temperature of operation of this process is limited by reactivity. If the temperature is too low, the yields are lower than desired. If the temperature is too high, the olefins tend to polymerize rather than react with the isoparaffins, and there is a tendency for oxidation to occur. This, of course, varies with the type of hydrocarbon feed and the acid strength. The optimum temperature range is considered to be between 30 and 50°F.

Contact of Reactants.—As in all reactions, the degree of contact of the reacting materials and the catalyst is one of the determining factors in the efficiency of the reaction. With poor contact, the acid consumption is high and the yield low. To achieve good contact, commercial installations utilize a pump-recycling-acid-hydrocarbon emulsion through jets or baffles.

Operation Troubles.—In all cases where a relatively complicated reaction is carried out in commercial-scale equipment with continuous flow, many difficulties may be encountered if sufficient control is not used. Probably the principal operation problem[37] is that of acid carry-over. Some of the factors causing this are rapid fluctuations in temperatures, acid levels, or acid-hydrocarbon ratio, too high an isoparaffin-olefin ratio, and bad acid. These factors can be controlled if sufficient care is exercised.

Yields.—The yield of alkylate based on the olefin charged varies from 175 per cent by weight to slightly over 200 per cent and depends upon several variables, of which the isoparaffin-olefin ratio is important. The higher this ratio, the higher the yield up to approximately a ratio of 7:1 or 8:1.

The yield of aviation fraction in the total product varies from 83 to 92 volume per cent.

Quality of Product.—In the flow diagram (Fig. 16-VI) the alkylate is taken from the bottom of the debutanizer tower. This material may and usually does contain hydrocarbons boiling at a higher temperature than that desired for the aviation blending fraction. Therefore, the alkylate from the debutanizer is usually fractionated into a light alkylate and heavy alkylate in an alkylate rerun tower. A typical[37a] alkylate yields the products with the characteristics tabulated in Table 17-VI.

TABLE 17-VI.—ALKYLATE FRACTIONS—QUALITY OF PRODUCT

	Light alkylate	Heavy alkylate
Yield, % vol..............	96.0	4.0
Gravity, A.P.I..............	68–69	48–52
Octane number, A.S.T.M.....	95	80–85
Distillation, Engler, A.S.T.M.:		
10%.....................	195°F.	
50%.....................	224°F.	
90%.....................	237°F.	
Vapor pressure, Reid, lb......	3.5–4	

Blending this light alkylate with a selected straight-run gasoline to give a gasoline of 86 octane number and adding 3 cc. of T.E.L. to the blend gives a gasoline of 100 octane number.

An aviation gasoline[36] produced by the blending of 50 per cent of light alkylate and 50 per cent of 77 octane number gasoline and 3 cc. of T.E.L. has the characteristics shown in Table 18-VI.

TABLE 18-VI.—AVIATION GASOLINE

Gravity, A.P.I...............................	71.8
Octane number clear (A.S.T.M.-C.F.R.)........	85
Octane number +3 cc. T.E.L................	100
Copper dish gum, mg./100 ml................	1
Acid heat, °F........................... ..	Below −76
Vapor pressure, Reid, lb.....................	7
Distillation, Engler, A.S.T.M.:	
50%, °F.................................	207
E.P., °F.................................	308

COMMERCIAL APPLICATION.—Six plants using the Sulfuric Acid Alkylation process were in operation in the early part of 1940, while eight others were under construction. The total capacity of the plants in operation and building was slightly over 12,000 bbl. per day. Since that time more have been built.

The Hydrofluoric Acid Alkylation Process.[39,41,42,43]—The most recent alkylation process to come into use is that which utilizes hydrofluoric acid as a catalyst. This method of manufacture of high-octane hydrocarbons is patented by the Universal Oil Products Co. under U.S. 2267730,[41] and the process is licensed by them. In this patent it is claimed that propenes, butenes, and pentenes, either singly or together, are alkylated effectively.

One of the principal advantages is the utilization of propene since the use of this material increases greatly the potential productive capacity for high-octane hydrocarbons over that attained by the use of butene alone as the olefin reactant, provided that sufficient isobutane is available.

CHEMISTRY OF PROCESS.—It is probable that the alkylation is catalyzed by hydrofluoric acid in the same manner as by sulfuric acid, namely, in two steps: the absorption step and the coupling step.   The following reactions show the mechanism.

```
                                           H
                                           HCH
         H   H  H                     H    |
         HC—C=CH  +  HF  ·       ·HC—C—F
         H                             H    H
           Propene                    Propyl fluoride

     H              H                 H    H
     HCH            HCH               HCH HCH
 H   |          |   H             H   |    |   H
 HC—C—F  +  HC—CH  ·    ·HC—C——C—CH  +  HF
 H   H          |   H             H   H    |   H
                HCH                        HCH
                H                          H
 Propyl fluoride   Isobutane           Isoheptane
```
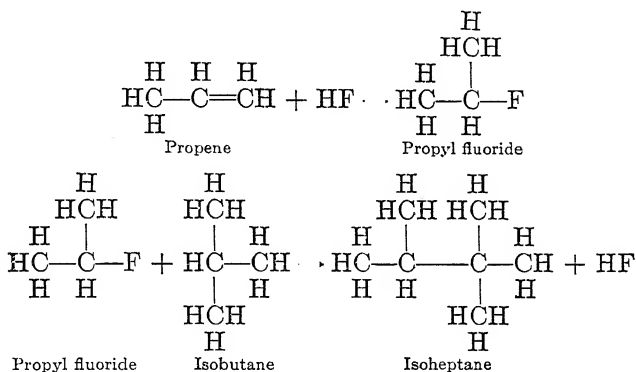
Similarly with butene and isobutane:

```
                                              H
                                              HCH
       H  H  H  H                    H    H   |
       HC—C—C=CH  +  HF  ·      ·HC—C—C—F
       H  H                          H    H   H
          Butene                     Butyl fluoride

     H              H                H    H
     HCH            HCH              HCH HCH
 H   H   |      |   H            H   |    |   H  H
 HC—C—C—F  +  HC—CH  ·   ·HC—C——C—C—CH  +  HF
 H   H          |   H            H   |    H  H
                HCH                       HCH
                H                         H
   Butyl fluoride   Isobutane    2,2,3-Trimethyl pentane
                                          (isooctane)
```
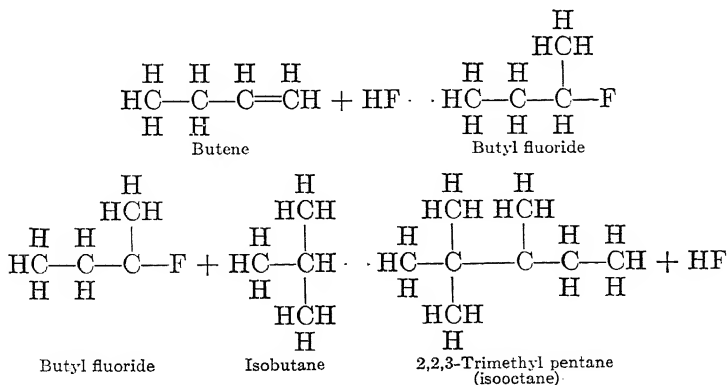
The reactions are exothermic and give off sufficient heat to require cooling of the reactants in order to keep the temperature in the desired range.

The alkyl fluorides, which are unreacted with the isobutane, are broken up by passing them over granular calcium fluoride or aluminum fluorides which decompose them into the corresponding olefins and HF, thus:

$$
\begin{array}{l}
\text{H} \\
\text{HCH} \\
\text{H} \qquad\qquad\qquad \text{H H H} \\
\text{HC—C—F} + \text{AlF}_3 \quad \cdot \text{HC—C=CH} + \text{HF} + \text{AlF}_3 \\
\text{H H} \qquad\qquad\quad \text{H} \\
\text{Propyl fluoride} \qquad\quad \text{Propene}
\end{array}
$$
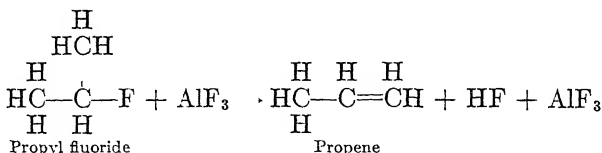
The mixture of olefin and free acid is passed over solid, granular sodium or potassium fluoride which form an addition compound with the acid.

$$
\begin{array}{l}
\text{H H H} \qquad\qquad\qquad\qquad \text{H H H} \\
\text{HC—C=CH} + \text{HF} + \text{NaF} \rightarrow \text{HC- -C=CH} + \text{NaF·HF} \\
\text{H} \qquad\qquad\qquad\qquad\qquad \text{H} \\
\quad \text{Propene} \qquad\qquad\qquad\qquad\quad \text{Propene} \qquad \text{Sodium-hydrogen} \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{fluoride}
\end{array}
$$
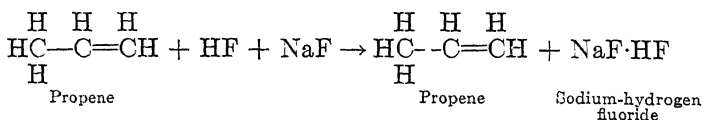
The hydrofluoric acid is recovered from the addition compound by heating.

$$\text{NaF·HF} + \text{heat} \rightarrow \text{NaF} + \text{HF}$$
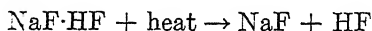
FLOW.—Figure 17-VI shows a simplified flow diagram for the Hydrofluoric Acid Alkylation process.

The essential equipment consists of a cooler in which the reaction takes place, a receiver in which the alkylate and unreacted hydrocarbons are separated from the HF, a fractionating system in which the alkylate is separated from the unreacted hydrocarbons, and a condensing-receiving system for these separated hydrocarbons.

The liquid isobutane and liquid HF are introduced separately into a line and mixed thoroughly by means of a pump. The butene or butene-isobutane is then introduced and the whole mixture passed into a cooler where the reactions are completed under controlled temperature conditions. The reacted mixture consisting of isoparaffins, olefins, and HF passes into a receiver in which the hydrocarbon-alkylate is separated from the HF. The hydrocarbon layer goes into a fractionating tower and the HF is recycled into the alkylation system. The fractionating tower (equipped with a reboiler) yields alkylate from the bottom and light hydrocarbons overhead. The alkylate goes to a caustic

scrubber to neutralize any acid present, and from the scrubber it goes to storage.

The light materials are condensed in a low-temperature condenser and are separated from any light gas that is formed during the reaction.   The light materials thus separated consist mainly of isobutane and are recycled into the alkylation system.

The unreacted alkyl fluorides which are formed are decomposed by passing over CaF_2 or AlF_3, forming HF and the olefin. The HF is removed by passing the mixture over NaF or KF
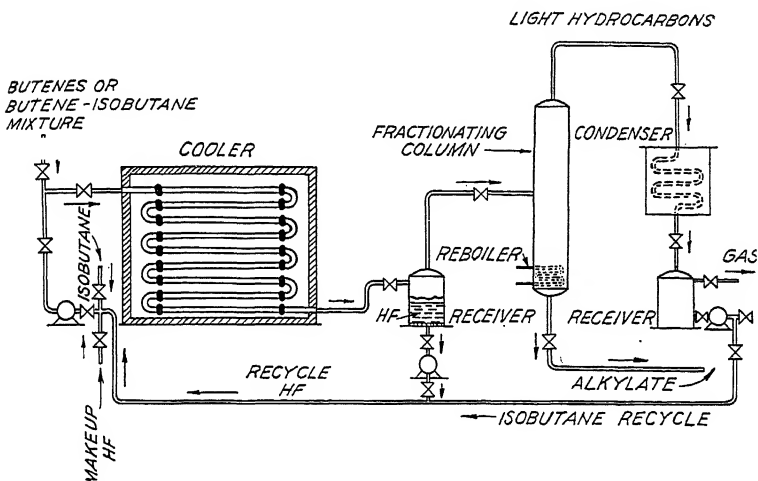
Fig. 17-VI.—Flow diagram of the Hydrofluoric Acid Alkylation process.
(*Courtesy of National Petroleum News.*)

which forms a combination salt from which the HF is recovered by heating.   The olefins are recycled.

ELEMENTS OF OPERATION.   *Feed Stocks.*—The olefin feed to the Hydrofluoric Acid Alkylation system may consist of propene, butene, or pentene, singly or in mixtures.   Propene is indicated as a major constituent of the olefin feed since it may be procured by dehydrogenation of propane, an abundant material.

The isoparaffin feed is essentially isobutane.   Probably isopentane can be used where sufficient amounts in excess of regular requirements are available.   (This is not specifically mentioned in the patent.)[41]

There is no definite statement in the patent as to the concentration of olefin and isoparaffin in the feed.   From the charac-

teristics of the reactions it is probable, however, that the following statements apply to this method of alkylation as well as the Sulfuric Acid method: (1) that the upper limit of concentration of olefin is determined by the tendency of the olefins to polymerize under the alkylation conditions, and (2) that the concentration is also dependent upon the effective ratio of isoparaffin to olefin desired for the reaction.

Isoparaffin—Olefin Ratio.—From the patent[41] the following experimental data are given:

Using a molal ratio of paraffin to olefin of 3:1, temperature from 20°–30°C. (68°–86°F.), and 100% hydrogen fluoride, 65% of the hydrocarbon product boiled within the octane range and 50% of this material was 2,2,4-trimethyl pentane. The percentage of fluorine in the total hydrogen products was 0.1%. Using a paraffin-olefin ratio of 1:3 and the same temperature and other operating conditions, 50% of the hydrocarbon products boiled above 200°C. (392°F.) and contained 5%–10% olefin polymers, indicating that over-alkylation and polymerization had taken place.

This indicates that for the operating conditions cited, at least, the optimum ratio of paraffin to olefin is that in which a higher proportion of paraffin is used. This follows since the reduction of the tendency for the olefin polymerization is effected by dilution.

Acid Strength and Consumption.—Data on experiments concerned with the effect of variation in acid strength on HF alkylation are given in the patent as follows:

To determine whether the anhydrous material and the water solutions of hydrogen fluoride could be used interchangeably or with substantially equivalent effects, tests were conducted using 100% anhydrous material, a 90% aqueous solution and a 75% aqueous solution. An approximately molal equivalent mixture of iso-butane and iso-butene was passed into the acids of varying concentration, at temperatures from 20°–30°C. (68–86°F.), the runs being made in a continuously stirred pressure autoclave.

Using 100% anhydrous hydrogen fluoride, the recovered hydrocarbon layer consisted of 50–60% octanes, of which about half was 2,2,4-trimethyl pentane. The hydrocarbon layer was completely saturated and contained only 0.1% of fluorine. With the 90% aqueous solution and a molal ratio of paraffin to olefin of 1.5:1, the hydrocarbon layer consisted of 48% octanes and there was present 1% of fluorine. With a

75% acid solution, an equivalent molal ratio of paraffin to olefin, and a temperature of 12°C. (53.6°F.) no alkylation occurred but there was considerable formation of butyl fluorides, iso-butenes forming tertiary butyl fluoride and normal butenes forming secondary butyl fluorides.

Thus, the experimental data reported indicate that it is necessary to use 100% anhydrous HF to secure the best results.

By use of the recovery system described above, it is claimed that there is little if any consumption of HF.

Temperature.—Again referring to the patent, the following discussion as to the effect of temperature on the Hydrofluoric Acid Alkylation process is given:

Using a mixture of iso-butane and iso-butene in a molal ratio of 1.5:1 and 100% hydrogen fluoride, best results were obtained at room temperature. At temperatures within the range of $-50°$ to $-60°C$. $(-58$ to $-76°F.)$ no alkylation occurred, but there was considerable polymerization of iso-butene. The hydrocarbon layer contained 2% fluorine. At a temperature of $+90°C$. (194°F.) utilizing sufficient pressure to maintain liquid phase and with a paraffin–olefin ratio of 1:3, the hydrocarbon products consisted of only 20% octanes and large amount of more highly alkylated derivatives. Temperatures as high as 100°C. (212°F.) may be used, if desired, by suitable adjustment of time factor, olefin-paraffin ratio and amount of catalyst used.

YIELDS AND QUALITY OF PRODUCT.—The yield of alkylate, using propene and isobutane, in hydrofluoric acid alkylation is claimed to approximate 1.7 gal. per gal. of propene plus approximately 1 gal. of isobutane. Using butene and isobutane the yield is claimed to be approximately the same. Based on the amount of acid used, the yield of alkylate per pound of acid is approximately 100 gal. per lb.

In general, the alkylate produced from both the propene-isobutane and butene-isobutane reaction has an octane number greater than 90. In experiments using isobutene and isobutane, at room temperature and 100 per cent HF, the alkylate consisted of approximately 50 per cent of isooctane.

COMMERCIAL APPLICATION.—The first commercial HF Alkylation plant was put in operation in December, 1942. There were several more to be built during 1943.

Thermal Alkylation.—The term *thermal alkylation* is applied to the process wherein selected olefin-paraffin mixtures are subjected to a temperature (900 to 1000°F.) bordering on the cracking

range and relatively high pressures (3,000 to 5,000 lb. per sq. in.). Under such conditions the combination of the constituents is effected without the use of a catalyst. The high pressure is necessary to counteract the cracking tendency at the temperature of operation. Olefins are polymerized readily under the conditions outlined but this polymerization is controlled by the relative concentration of olefin and paraffin hydrocarbons in the reaction zone. Thus, in order to react the olefins with the paraffins, the concentration of olefins must be low and that of the paraffins high.

Thermal alkylation reacts ethene readily, propene and the n-butene less easily, and isobutene with difficulty. n-Pentane, isopentane, n-butane, isobutane, and propane all react readily in this process. Methane and ethane react with difficulty.

The principal thermal alkylation process of commercial interest at present is the Neohexane process of the Phillips Petroleum Co.

NEOHEXANE-THERMAL ALKYLATION PROCESS.[44]—The Neohexane process, developed by the Phillips Petroleum Co., is a thermal alkylation process which is capable of utilizing lower olefins and n- and isoparaffins in reactions producing hydrocarbons of high-antiknock value and good volatility characteristics.

CHEMISTRY OF PROCESS.—In thermal alkylation the products formed depend on several factors, among which temperature, pressure, and composition of feed are important. Oberfell and Frey,[44] describing the Neohexane process, state that by careful selection of the individual paraffins and olefins, primary reaction products result from the union of one molecule of each, accompanied by secondary reaction products. A list of reactions is given below which indicates the principal product formed under controlled conditions of feed, temperature, and pressure.

| Ethene | Propane | Isopentane | n-Pentane |

$$\underset{\text{Ethene}}{\overset{\text{H H}}{\underset{\text{H H}}{C=C}}} + \underset{n\text{-Butane}}{\overset{\text{H H H H}}{\underset{\text{H H H H}}{HC-C-C-CH}}} \rightarrow \underset{3\text{-Methyl pentane}}{\overset{\overset{\text{H}}{\overset{\text{HCH}}{}}}{\overset{\text{H H | H H}}{\underset{\text{H H H H H}}{HC-C-C-C-CH}}}}$$

$$\underset{\text{Ethene}}{\overset{\text{H H}}{\underset{\text{H H}}{C=C}}} + \underset{\text{Isobutane}}{\overset{\overset{\text{H}}{\overset{\text{HCH}}{}}}{\overset{\text{| H}}{\underset{\text{| H}}{\underset{\overset{\text{HCH}}{\text{H}}}{HC-CH}}}}} \rightarrow \underset{\substack{2,2\text{-Dimethyl butane}\\ \text{(neohexane)}}}{\overset{\overset{\text{H}}{\overset{\text{HCH}}{}}}{\overset{\text{H H | H}}{\underset{\text{H H | H}}{\underset{\overset{\text{HCH}}{\text{H}}}{HC-C-C-CH}}}}}$$

$$\underset{\text{Propene}}{\overset{\text{H H H}}{\underset{\text{H H}}{HC-C=C}}} + \underset{\text{Propane}}{\overset{\text{H H H}}{\underset{\text{H H H}}{HC-C-CH}}} \rightarrow \underset{2,3\text{-Dimethyl butane}}{\overset{\overset{\text{H H}}{\overset{\text{HCH HCH}}{}}}{\overset{\text{H | | H}}{\underset{\text{H H H H}}{HC-C-C-CH}}}}$$

or

$$\underset{2\text{-Methyl pentane}}{\overset{\text{H H H H H}}{\underset{\overset{\text{HCH}}{\text{H}}}{\underset{\text{H | H H H}}{HC-C-C-C-CH}}}}$$

$$\underset{\text{Ethene}}{\overset{\text{H H}}{\underset{\text{H H}}{C=C}}} + \underset{\text{Cyclohexane}}{H_2C} \cdots \rightarrow \cdots \underset{\text{Ethyl cyclohexane}}{H_2C}$$

These reactions are given to show the formation of the principal
product.   Actually, many other reactions take place and the
separation of the desired pure hydrocarbon in most cases requires
a highly efficient fractionation system.

FLOW.—A diagrammatic flow sheet of the Neohexane Thermal
Alkylation process is shown in Fig. 18-VI.   This flow diagram
describes the pilot-plant operation from which the data given
in the following pages were derived.   This also was the projected
flow for the plant process installed in January, 1940.

The principal equipment for the process consists of the follow-
ing: cracking furnace, compressors, ethene absorber (in which the

ethene is absorbed by part of the isobutane charge), high-pressure charging pumps, thermal alkylation furnace, and the isobutane-neohexane gasoline fractionator.

The process operates as follows: The feed to the cracking furnace, consisting of ethane, propane, and butane, or mixtures of them, is cracked at a high temperature (around 1425°F.) and a pressure just a few pounds above atmospheric, thereby favoring
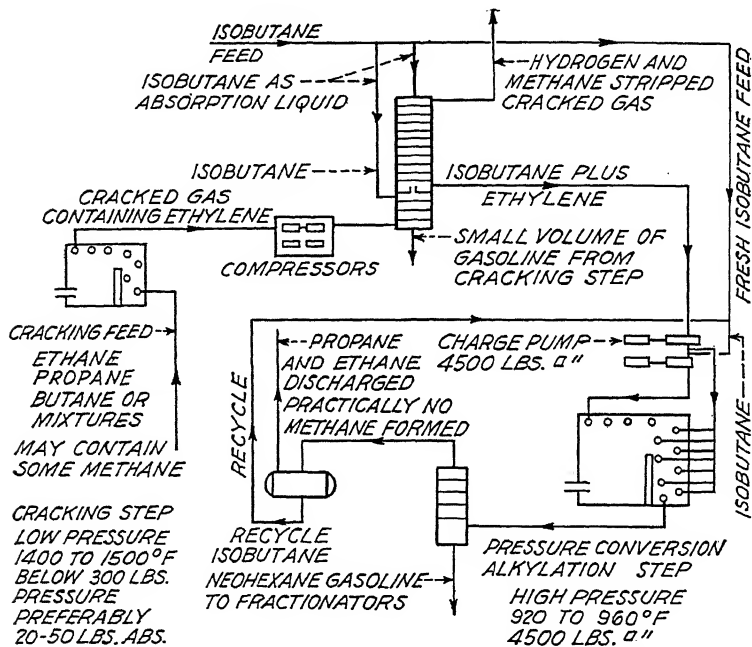
FIG. 18-VI.—Flow diagram of the Neohexane or Thermal Alkylation process.
(*Courtesy of Refiner Natural Gasoline Mfr.*)

the formation of ethene. The cracked gases are then cooled, compressed, and passed into the lower part of an absorption tower wherein they are absorbed by isobutane, part of which is fed into the top of the tower to scrub the lighter gases and part about one-third of the way up from the bottom. This tower yields hydrogen and methane from the top, materials heavier than the ethene-isobutane mixture from the bottom (gasoline from cracking and polymerization), and the isobutane-ethene mixture from the middle. This mixture is pumped at 4,500 lb. per sq. in. pressure into a manifold which distributes it among

10 inlets situated along a tube coil in the alkylation furnace, which constitutes the reaction zone. Fresh isobutane feed of greater volume than that of the isobutane-ethene mixture is preheated in a preheater coil to a temperature of 950°F. and continuously pumped into the reaction coil into which the 10 inlets feed. The alkylation products are separated in a fractionating separator from which the isobutane (unused) and lighter materials are taken overhead and the neohexane gasoline fraction removed from the bottom of the tower. The bottom fraction is further fractionated to separate the boiling range of product desired. The overhead is further separated into isobutane, which is recycled into the fresh isobutane feed, and lighter products such as ethane and propane which are withdrawn from the system.

ELEMENTS OF OPERATION. *Feed Stocks.*—The Thermal Alkylation process will react normal paraffins as well as isoparaffins with the olefins. For neohexane manufacture the charge must consist of relatively pure olefin and paraffin hydrocarbons but, when it is desired to produce a motor fuel of relatively wide boiling range, it is possible to use mixtures of paraffins and mixtures of olefins of less purity.

The olefins are produced from cracking a mixture of 1-, 2-, 3-, and 4-carbon paraffins at 1425°F. and a few pounds above atmospheric pressure. The *n*-paraffins may be secured from natural gasoline, refinery gases, etc. The isobutane used for the manufacture of neohexane may be procured from natural gasoline, refinery gases, and isomerization of *n*-butane.

Since normally, under the conditions favoring thermal alkylation, the olefins polymerize with themselves readily, it is necessary to keep the proportion of paraffins to olefins in the reaction zone high. This dilutes the olefins and causes the olefin-paraffin combination rather than the olefin-olefin polymerization.

In the pilot plant operation reported on by Oberfell and Frey, the following olefin-paraffin proportions in the feed were used:

> Ethene:propane::8.9:91.1
> Ethene:propane::25.0:75.0
> Propene:propane::12.8:87.2
> Ethene:isobutane::11.8:88.2
> Ethene:isobutane::25.6:74.4
> Isobutene:isobutane::8.2:91.8
> Ethene:cyclohexane::12.5:87.5

The proportions range from approximately 3:1 to approximately 10:1. The ethene-isobutane ratios, which are of principal interest in the manufacture of neohexane, range from 1:3 to 1:7.

Operating Conditions.—Oberfell and Frey described the pilot-plant operation on various feed stocks under the conditions listed in Table 19-VI.

TABLE 19-VI.—THERMAL ALKYLATION—CONDITIONS OF OPERATION

Reactants	% wt.	Pressure, lb.	Temperature, °F.	Total reaction time, min.	Total gasoline yield, % by wt.
C_2H_4 C_3H_8	8.9 91.1	4,500	950	4.1	11.2
C_2H_4 C_3H_8	25 75	4,500	950	5.6	32.8
C_3H_6 C_3H_8	12.8 87.2	6,300	943	7.4	20.5
C_2H_4 iC_4H_{10}	11.8 88.2	4,500	959	2.2	14.8
C_2H_4 iC_4H_{10}	25.6 74.4	4,500	941	4.0	35.4
iC_4H_8 iC_4H_{10}	8.2 91.8	8,000	907	3.2	2.9
C_2H_4 Cyclohexane	12.5 87.5	4,500	923	3.9	22.5*

* Liquids other than cyclohexane.

YIELDS.—Table 20-VI gives the analysis on liquid alkylates formed in the two ethene-isobutane reactions described in Table 19-VI.

The yield of neohexane based on the original charge is, for the 11.8:88.2 ratio, 6.26 per cent by weight and, for the 25.6:74.4 ratio, is 11.1 per cent by weight. The amount of heavy polymer formed is shown to be approximately eight times greater for the lower isoparaffin-olefin ratio.

QUALITY OF PRODUCT.—The neohexane produced by thermal alkylation can be separated from the other hydrocarbons formed

by fractional distillation, since its boiling point is separated from those of adjacent hydrocarbons by considerable intervals. It has the properties listed in Table 21-VI.

TABLE 20-VI.—COMPOSITION OF LIQUID ALKYLATES

Reactants	C_2H_4	iC_4H_{10}	C_2H_4	iC_4H_{10}
Per cent	11.8	88.2	25.6	74.4
Yield, %, liquid	14.8		35.4	
C_5H_{10}	1.9		2.2	
iC_5H_{12}	5.0		3.1	
nC_5H_{12}	5.0		2.7	
C_6H_{12}	5.2		2.7	
2,2-Dimethyl butane	42.1		31.3	
2,3-Dimethyl butane	17.5		9.9	
2-Methyl pentane	17.5		9.9	
n-Hexane	17.5		9.9	
C_7H_{14}	2.4		2.0	
C_7H_{16}	4.1		4.1	
C_8H_{16}	3.2		2.9	
C_8H_{18}	12.7		13.7	
C_9 to 392°F	4.8		17.4	
Heavier than 392°F	1.1		8.0	

TABLE 21-VI.—PROPERTIES OF NEOHEXANE

Boiling point, °F	121.5
Freezing point, °F	−144.8
Gravity, A.P.I.	84.9
Gravity specific	0.6494
Octane number, A.S.T.M.	94
Refractive index, $nD20°C$	1.36887
Vapor pressure, lb./sq. in	5.9

Neohexane +3.0 cc. T.E.L. per gal. is equal in antiknock value to c.p. isooctane, having an octane number of 100, and it is claimed to have a higher lead susceptibility than isooctane.

The alkylate produced from pilot-plant-scale thermal alkylation of isobutane by ethene has the properties shown in Table 22-VI.

COMMERCIAL APPLICATION.—At least one large-scale plant was in operation at the latter part of 1942 utilizing the Thermal Alkylation process.

TABLE 22-VI.—PROPERTIES OF ALKYLATE FROM THERMAL ALKYLATION

Distillation A.S.T.M.	Debutanized Alkylate
Initial, °F	118
5%, °F	129
10%, °F	136
20%, °F	142
30%, °F	146
40%, °F	151
50%, °F	157
60%, °F	166
70%, °F	180
80%, °F	206
90%, °F	268
E.P., °F	370
Gravity, A.P.I.	73.2
Octane number, A.S.T.M.	82.5
Vapor pressure, Reid, lb.	7.6

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CHAPTER VII

PRODUCTION OF FINISHED AVIATION GASOLINES

In the preceding chapters we have studied the manufacturing methods and processes involved in making or producing various types of stocks to be utilized as components of aviation gasoline. Because of the properties such as octane number, chemical stability, volatility with low vapor pressure, low sulfur content, and low freezing point required in the finished fuel, it is necessary to blend several materials to achieve the quality desired. This is particularly true of the higher octane grades. The combinations of the various processing elements to produce satisfactory aviation gasolines and the effects of the characteristics of the individual components on the finished gasolines are discussed in this chapter.

In Chap. III we learned that there are three principal types of aviation gasoline being produced at the present time. These are the 73, 91, and 100 octane grades and with the exception of octane number, maximum permissible tetraethyl lead content, and calorific value, the qualities specified for all three are the same. These properties are listed in Table 1-VII.

Since most of the characteristics are identical for all grades of aviation gasoline, it would appear that the same base stock could be used for the manufacture of all types and the higher octane grades could be produced by merely the addition of greater quantities of tetraethyl lead. This is not true, unfortunately, because the amounts of lead required in practically all cases to produce 100 octane fuel would exceed the specified limits, and therefore other materials must be used in the blends. The need for high-octane blending components has given rise to the various processes described in Chaps. V and VI. With so many types of processing available both for the production of aviation base stocks and high-octane blending materials, many different process combinations are used for the production of aviation gasolines.

It is not possible for us to consider in this book all the possible combinations of processes in use today and their details, since

TABLE 1-VII.—SPECIFICATIONS ON AVIATION GASOLINE[1]

	Grade		
	73	91	100
Octane number,* min................	73	91	100
Tetraethyl lead, cc./gal., max.........	1.0	4.0	3.0
Calorific value, net, B.t.u./lb., min....	18,300	18,700	18,700

Corrosion, copper dish.........................	None
Corrosion, copper strip.........................	None
Distillation, A.S.T.M.:	
10% evap., °F., max.........................	158
50% evap., °F., max.........................	212
90% evap., °F., max.........................	257
10% + 50% evap., °F., min.................	307
Recovery, %, min...........................	97.0
Residue, %, max...........................	1.5
Loss, %, max..............................	1.5
Acidity of residue.........................	None
Freezing point, °F., max......................	−76
Gum, copper dish, mg./100 cc., max............	5.0
Gum, accelerated, mg./100 cc., max............	6.0
Gum inhibitor, lb./5,000 gal., max.............	1.0
Sulfur, %, max...............................	0.05
Vapor pressure, Reid, lb., max................	7.0
Water miscibility, max.......................	±2 ml.

* A.S.T.M.-C.F.R. Aviation method.

there are probably as many variations in procedure as there are refiners manufacturing aviation gasoline. The processing arrangements shown on the following pages, therefore, are those most commonly used and are based on the principal methods producing the various blending components.

73 OCTANE GRADE AVIATION GASOLINE

The 73 octane aviation gasoline is the "third-grade" fuel of aviation. Although no recent figures are available on the quantity of this grade produced compared to the other grades, it is probable that it is 10 per cent or less. In 1940 the estimated average octane requirement of commercial users was around 91 and the major requirements were for the 87 to 100 octane grades.

It is probable in the near future that all aviation fuel will be above 90 octane number.

The 73 octane grade aviation fuel is the least difficult to produce of the three present grades. Typical compositions are shown in Table 2-VII.

TABLE 2-VII.—TYPICAL COMPOSITIONS OF 73 OCTANE GRADE AVIATION GASOLINE

	Composition		
Depentanized natural gasoline, 60–70 octane number, %	80–90		25–50
Straight-run naphtha, 60–70 octane number, %		80–90	50–75
Isopentane fraction, 90–95 octane number, %	10–20	10–20	10–20
Tetraethyl lead, cc./gal	0–1.0	0–1.0	0–1.0
Gum inhibitor, lb./5,000 gal			

The three principal methods for production of 73 octane aviation gasoline are as follows:

1. Blending a stabilized straight-run naphtha, 80 to 90 per cent, with isopentane, 10 to 20 per cent, and adding not more than 1 cc. of tetraethyl lead per gallon. The naphtha should have an approximate boiling range of 100 to 300°F., an octane number of 60 to 70, and a total sulfur content of 0.05 per cent or less. This will make a satisfactory aviation-fuel blend if the vapor pressure requirement is obtained by adjusting the amount of isopentane used.

2. Blending a depentanized natural gasoline, 80 to 90 per cent, with isopentane, 10 to 20 per cent, and adding tetraethyl lead not exceeding 1 cc. per gal. The boiling range of the depentanized natural gasoline should be adjusted to 100 to 300°F. and the octane number, to 60 to 70. This type of blend, in general, results in a more volatile fuel than that made from straight-run naphthas.

3. Blending a depentanized natural gasoline, 25 to 50 per cent, with a straight-run naphtha, 50 to 75 per cent, isopentane, 10 to 20 per cent, and adding not more than 1 cc. of tetraethyl lead per gallon. The boiling ranges of the base stocks should approximate 100 to 300°F.

The method utilizing light straight-run naphtha as the base stock is most commonly used. However, since in most cases where aviation fuel is being manufactured it is necessary to recover quantities of isopentane from natural gasoline, it is economical to blend the depentanized "natural" with the straight-run stock. This gives a more volatile finished gasoline and usually imparts a slightly higher octane number to the base
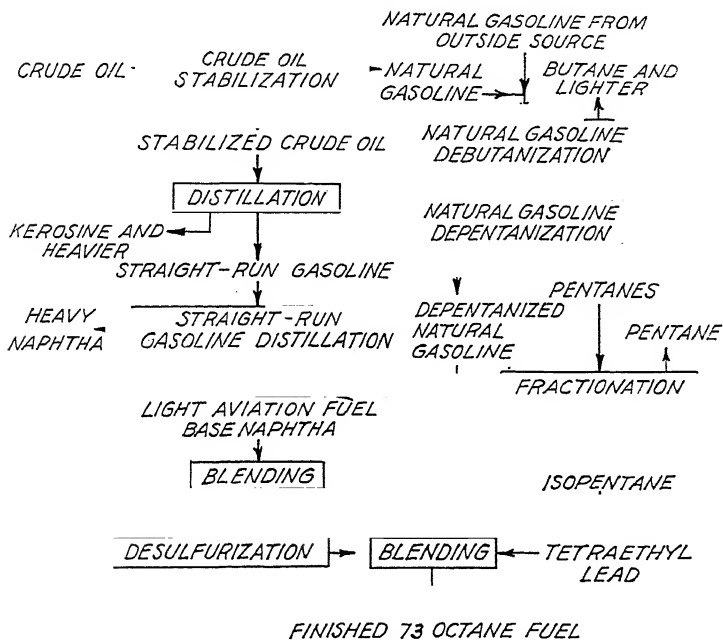
FIG. 1-VII.—73 octane grade aviation fuel from straight-run naphtha and natural gasoline.

blend. By careful fractionation in preparation of the base naphtha it is possible to produce a stock of the correct vapor pressure containing no butane, thus eliminating the necessity for isopentane addition.

Cody and Luntz[2] investigated the possibility of making 91 octane grade aviation fuel from an East Texas natural gasoline by close fractionation, reblending the isopentane, and "leading." Although the production of the 91 octane grade was possible only under certain conditions, the 73 grade could be made without difficulty. Pertinent data are shown in Table 3-VII.

TABLE 3-VII.—AVIATION GASOLINE FROM EAST TEXAS NATURAL GASOLINE

	18 lb.	26 lb.
Yield, vol. %, based on natural gasoline..	65.6	32.0
Octane number,* clear..................	60.3	70.4
Octane number* + 1 cc. T.E.L./gal......	75.7	83.2

* A.S.T.M.-C.F.R. Motor method.

Process Outline—73 Octane Grade.—The method of producing the 73 octane grade aviation fuel shown in Fig. 1-VII utilizes both straight-run naphtha and depentanized natural gasoline. The volatility range of the stocks should be roughly 100 to 300°F. and the sulfur content should be reduced to approximately 0.05 per cent. The degree of stabilization of the stocks defines the amount of isopentane necessary to blend with those stocks in order to achieve the correct vapor pressure. This is a combination arrangement and indicates the usual steps necessary in preparing the blending stocks. In utilizing either base separately, the steps are the same as shown in Fig. 1-VII.

91 OCTANE GRADE AVIATION GASOLINE

The 91 octane grade aviation fuel may be considered the "regular" grade of aviation gasoline. Large quantities of this

TABLE 4-VII.—TYPICAL COMPOSITIONS OF 91 OCTANE GRADE AVIATION GASOLINE

Composition

Straight-run naphtha, 65–80 octane number, %	30–50	30–50	30–50	60–80
Conversion naphtha,* 76–82 octane number, %	50–70		25–35	
Isomerized naphtha,† 75–80 octane number, %		50–70	25–35	
Benzol, 90–100 octane number, %				10–15
Isopentane, 90–95 octane number, %	0–10	0–10	0–10	10–15
Tetraethyl lead, cc./gal., max...........	4	4	4	4
Gum inhibitor, lb./5,000 gal., max......	1	1	1	1

* From catalytic cracking, gas reversion, polyforming, hydroforming, etc.
† From naphtha isomerization or natural gasoline isomerization.

material have been and are being used by both commercial and government services. Under present conditions the amount of this type of fuel produced is less than that of the 100 octane grade and the extensive facilities developed by the industry to supply the higher grade aviation gasoline to fulfill the increased war demands probably will enable, at the end of the war, the production of 100 octane fuel at such a cost that it will replace most of the 91 octane grade.

This grade of aviation gasoline is a blend whose composition depends upon the types of blending components utilized and their individual characteristics as well as their blending characteristics.

Compositions of typical blends are shown in Table 4-VII. The compositions indicated vary with the type, amount, and characteristics of the base stocks.

As shown in Table 4-VII, suitable 91 octane aviation fuel may be the result of one of several different compositions. The principal blends are as follows:

1. A stabilized straight-run naphtha, 30 to 50 per cent, blended with a debutanized conversion naphtha, 50 to 70 per cent, 0 to 10 per cent of isopentane, and containing not more than 4 cc. of tetraethyl lead per gallon. The naphtha stocks should boil roughly within the range of 100 to 300°F., have sufficient lead susceptibility to meet the octane number requirement, and be stable toward oxidation. Gum inhibitor in the quantity not exceeding 1 lb. per 5,000 gal. may be added. The amount of isopentane added, if any, is dependent upon the vapor pressure of the naphtha stocks.

2. A stabilized straight-run naphtha, 30 to 50 per cent, blended with a naphtha or natural gasoline isomate, 50 to 70 per cent, and containing not more than 4 cc. of tetraethyl lead per gallon. Isopentane may be added to the extent of 0 to 10 per cent if necessary, to meet vapor pressure specifications. The stocks should boil within 100 to 300°F., have good lead susceptibilities, and be stable. Gum inhibitors may be added not exceeding 1 lb. per 5,000 gal. although usually in this type of blend it is not necessary, owing to the stable character of the stocks.

3. A blend of straight-run naphtha, 30 to 50 per cent, conversion naphtha, 25 to 35 per cent, and isomate, 25 to 35 per cent, with 4 cc. of tetraethyl lead added. Isopentane may be

used to the extent of 0 to 10 per cent in the blend to produce the correct vapor pressure.

4. A blend of straight-run naphtha, 60 to 80 per cent, with benzol, 10 to 15 per cent, and isopentane, 10 to 15 per cent, con-
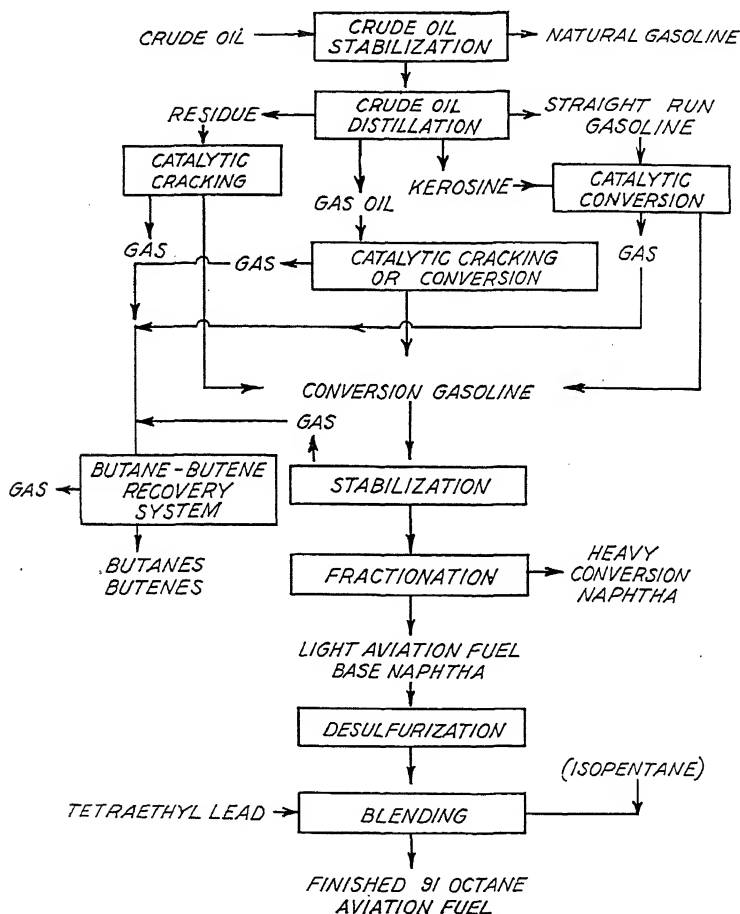
FIG. 2-VII.—Flow arrangement for production of 91 octane grade aviation gasoline from catalytic conversion naphthas.

taining 4 cc. of tetraethyl lead per gallon. Isopentane is usually necessary in this type of blend to produce the specified vapor pressure. The quantity of benzol is limited because of its high freezing point.

In addition to the above blends, it is possible to utilize any one of the high-octane conversion stocks alone with the addition of tetraethyl lead.   This is not the most common practice since, where possible, it is usually attempted to blend as much of the relatively cheaper straight-run naphtha as is feasible.   The
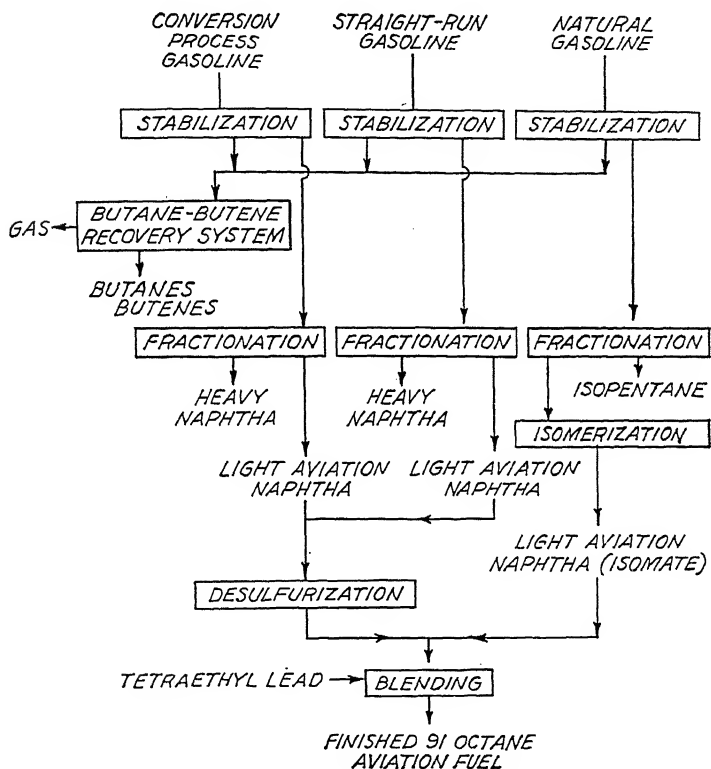
FIG. 3-VII.—Flow arrangement for production of 91 octane grade aviation gasoline by blending conversion and straight-run naphthas and converted natural gasoline.

quantity that can be blended depends primarily upon the octane number and lead susceptibility of the straight-run naphtha.

In certain other cases, where a straight-run naphtha or depentanized natural gasoline of 75 to 80 octane number is available, the addition of the maximum amount of lead permitted and isopentane may be sufficient to produce a satisfactory fuel of 91 octane number.

The various conversion naphthas in general have high-octane numbers and good lead susceptibilities. In some cases[3,4] in order to meet the gum stability specifications, it is necessary to process these stocks with clay treatment or acid treatment to reduce the olefin content.

Process Outlines—91 Octane Grade.—The process outlines shown in Figs. 2-VII to 4-VII are schematic and include possible
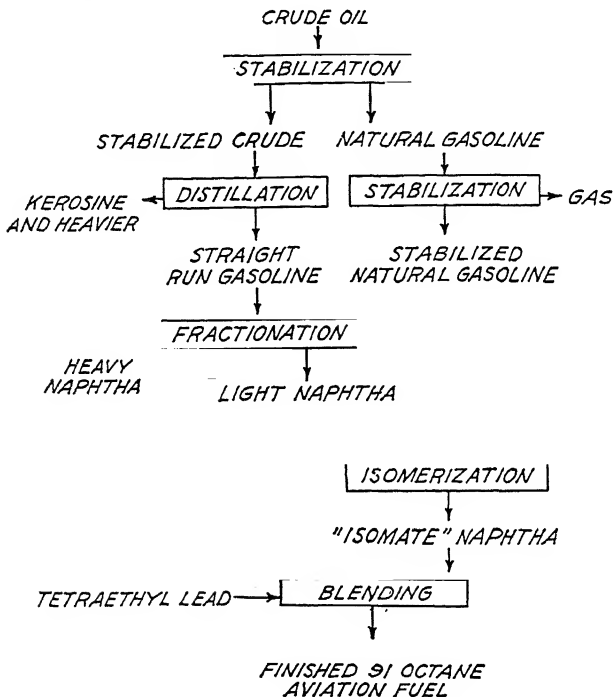
Fig. 4-VII.—Flow arrangement for the production of 91 octane grade aviation gasoline by isomerization.

combinations of processes to produce the 91 octane grade fuel. Figure 2-VII shows a diagram wherein such processes as catalytic cracking, gas reversion, and polyforming, are combined to yield a naphtha that, when leaded, is a suitable aviation fuel. Figure 3-VII illustrates a flow arrangement wherein conversion naphtha, straight-run naphtha, and isomate are combined to produce the aviation gasoline. Figure 4-VII illustrates the type of flow utilized in procuring 91 octane aviation gasoline from isomerization.

In all the flow diagrams shown, only the rough outlines are indicated. These are offered merely as type studies and many alternative combinations are possible.

100 OCTANE GRADE AVIATION GASOLINE

Since 1935 the importance of 100 octane or "premium" grade aviation gasoline has been increasing greatly every year. Its production has grown from a few thousand gallons per year to several billion gallons per year and, by the latter part of 1941, the production rate was approximately equal to that of the premium grade motor fuel in normal times.[5] This enormous production is due mainly to military demands brought on by a war that is principally an air war. However, since the refining industry is increasing its capacity enormously and experience in process operation and extended research will further reduce production costs, it is highly probable that this type of fuel will become a general standard for all aviation and that its production rate will be still further increased after the war.

The 100 octane aviation gasoline at present is a blend of several components whose type and amount depend upon their individual and blending characteristics. The first gasoline of this type was composed of (1) a straight-run base stock of relatively high octane number (70 to 75), (2) isoctane or isooctane mixtures, (3) isopentane, and (4) tetraethyl lead. Recent developments in both the manufacture of high-octane-number base stocks and high-octane-number hydrocarbons have changed the character of the blending components until only isopentane and tetraethyl lead are certain to be found in the finished fuel.

At present, 100 octane aviation gasoline may be classified according to the type of high-octane hydrocarbon blending component which it contains. On this basis there are four classifications:

1. Alkylate gasoline.
2. Hydrogenated polymer gasoline.
3. Neohexane gasoline.
4. Substituted aromatic type gasoline.

In alkylate gasolines there are contained high-octane alkylates ranging from 90 to 100 octane and procured from such processes as Sulfuric Acid alkylation, and Hydrofluoric Acid alkylation. In the hydrogenated polymer gasolines are found the isooctanes

from hydrogenation of the materials from such selective polymerization processes as Sulfuric Acid, Phosphoric Acid, and Copper Pyrophosphate. Neohexane aviation gasoline contains neohexane obtained from the Thermal Alkylation process. In the substituted aromatic-type gasolines the principal high-octane blending component is a material such as isopropyl benzene, or isobutyl benzene from alkylation or polymerization processes. This type is relatively new and very little information is available upon either the processes involved in manufacturing the compounds or their percentages utilized in the finished aviation fuel.

100 octane aviation gasoline may also be classified according to the type of base stock used in its composition, as follows:

1. Straight-run naphtha base.
2. Conversion naphtha base.
3. Mixed base.

TABLE 5-VII.—TYPICAL COMPOSITIONS OF 100 OCTANE GRADE AVIATION GASOLINES

	Compositions				
	1	2	3	4	5
Straight-run naphtha, 65–80 octane number, %....................	30–50	30–50	.....	30–40	30–50
Conversion naphtha, 76–82 octane number, %....................	.....	....	40–60	30–40	
Isopentane, 90–95, octane number, %	10–15	10–15	10–15	10–15	10–15
Neohexane, 90–95, octane number, %	.....	20–30			
Isooctanes,* 90–100 octane number, %........................	40–60	20–30	30–40	30–40	30–50
Benzene, 90–100 octane number, %..	.....	.....	.....	.....	10–15
Tetraethyl lead, cc./gal., max........	3.0	3.0	3.0	3.0	3.0
Gum inhibitor, lb./5,000 gal., max....	1.0	1.0	1.0	1.0	1.0

* Alkylates, alkylate gasolines, hydrogenated polymers.

The straight-run naphtha base was the first conventional type utilized and still represents a major portion of the gasoline produced. The advent of conversion processes such as catalytic cracking, isomerization, Hydroforming, and Gas Reversion, has enabled the production of high-octane base stocks (in some cases

requiring some treatment to achieve stability) which are satisfactory for the production of 100 octane aviation gasoline.   The mixed base is composed of straight-run and conversion naphthas, their relative percentages depending upon the practice of the individual refiner.
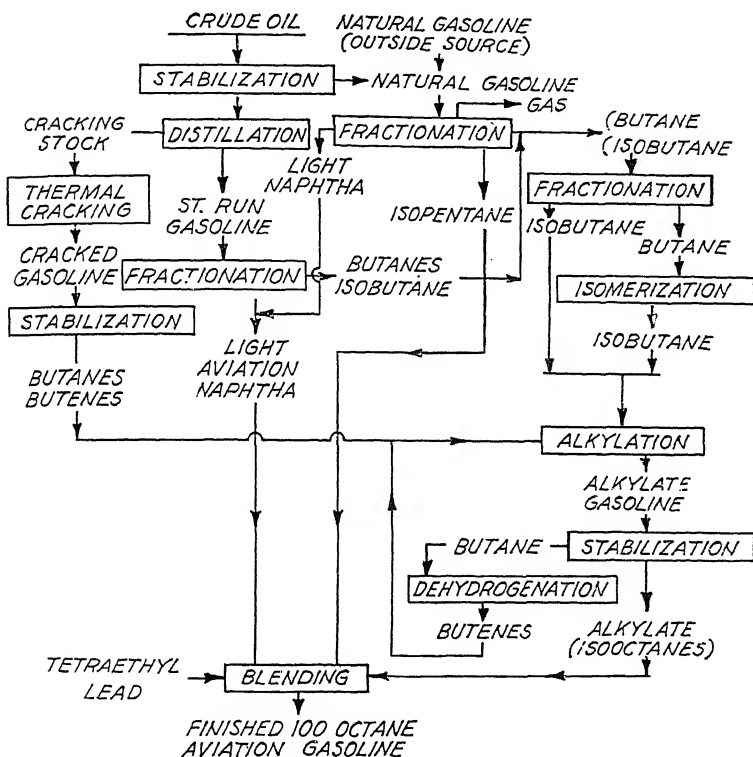
FIG. 5-VII.—Production of 100 octane aviation gasoline from straight-run base stock and alkylate.

It is evident, therefore, that the number of different types of gasoline possible to produce by combining the different high-octane blending agents and base stocks is enormous, and it would indeed be difficult to list all the possible compositions.   In order to give an idea of the amounts of the various components used in 100 octane fuel, Table 5-VII is presented listing several typical compositions giving the usual percentage range of the various blending materials.

The specifications which this premium grade aviation fuel must meet are the same as those for the 91 octane grade with the exception that the minimum octane number requirement is 100 and the maximum permissible tetraethyl lead content is 3 cc. per gal. instead of 4 cc. The higher octane number requirement and the reduced permissible lead content are responsible for the more complicated processing technique necessary to produce a satisfactory product. The general procedures followed in com-
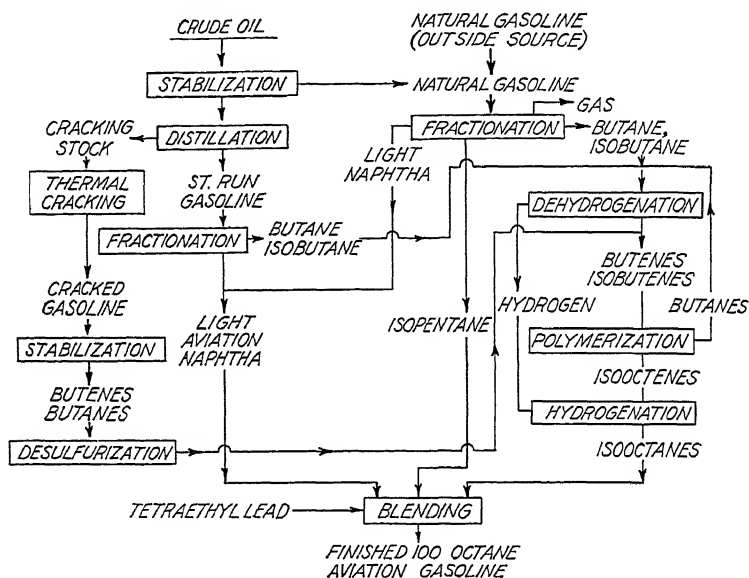
Fig. 6-VII.—Production of 100 octane aviation gasoline from straight-run base stock and hydrogenated polymer.

pounding a finished 100 octane aviation gasoline are given as follows:

1. Blending a suitable boiling range (100 to 300°F.) straight-run naphtha, 30 to 50 per cent, with isooctanes, 40 to 60 per cent, and isopentane, 10 to 15 per cent, and adding tetraethyl lead in amount not exceeding 3 cc. per gal.

2. Blending a high-octane conversion naphtha, 40 to 60 per cent, with isooctanes, 30 to 40 per cent, and isopentane, 10 to 15 per cent, and "leading" with 3 cc. of tetraethyl lead.

3. Blending straight-run naphtha, 30 to 40 per cent, with a high-octane conversion naphtha, 30 to 40 per cent, isopentane,

10 to 15 per cent, and isooctanes, 30 to 40 per cent, and "leading" with a maximum of 3 cc. of tetraethyl lead per gallon.

4. Blending a straight-run naphtha, 30 to 50 per cent, with neohexane, 20 to 30 per cent, isooctanes, 20 to 30 per cent, and isopentane, 10 to 15 per cent, and "leading" with not more than 3 cc. of tetraethyl lead per gallon.

5. Substituting various high-antiknock aromatic compounds such as benzene and the benzenes containing saturated side
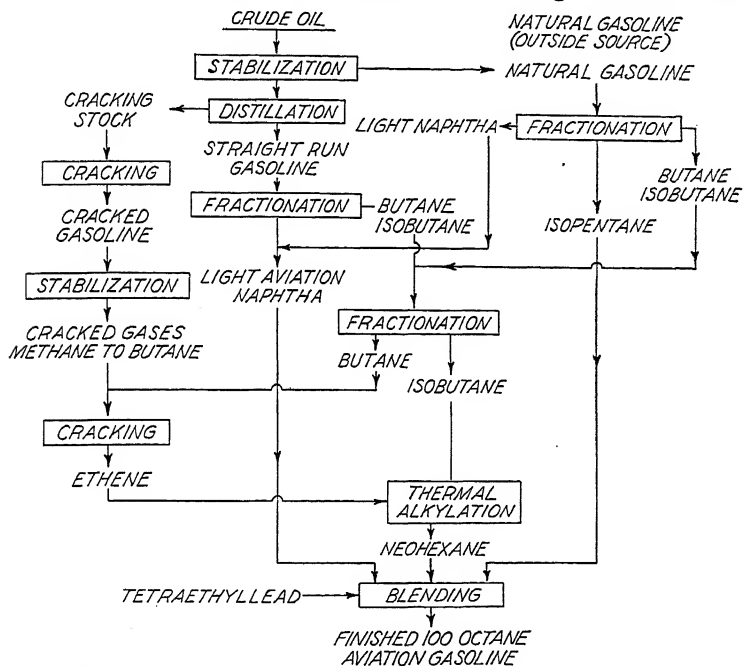
FIG. 7-VII.—Production of 100 octane aviation gasoline from straight-run base stock and neohexane.

chains such as cumene and isobutyl benzene, for a portion of the aliphatic high-antiknock hydrocarbons used in the foregoing blends.

These blending procedures are general and not intended to indicate the exact components or the quantities to be used since they vary with the processes available to the refiner and the stocks produced as well as the individual characteristics of the stocks. The effect of the properties of the components on the finished fuel is discussed later in this chapter.

Process Outlines—100 Octane Grade.—Figures 5-VII to 8-VII are schematic diagrams showing common process arrangements for the production of 100 octane aviation gasoline. These are intended to give possible combinations based on each type of
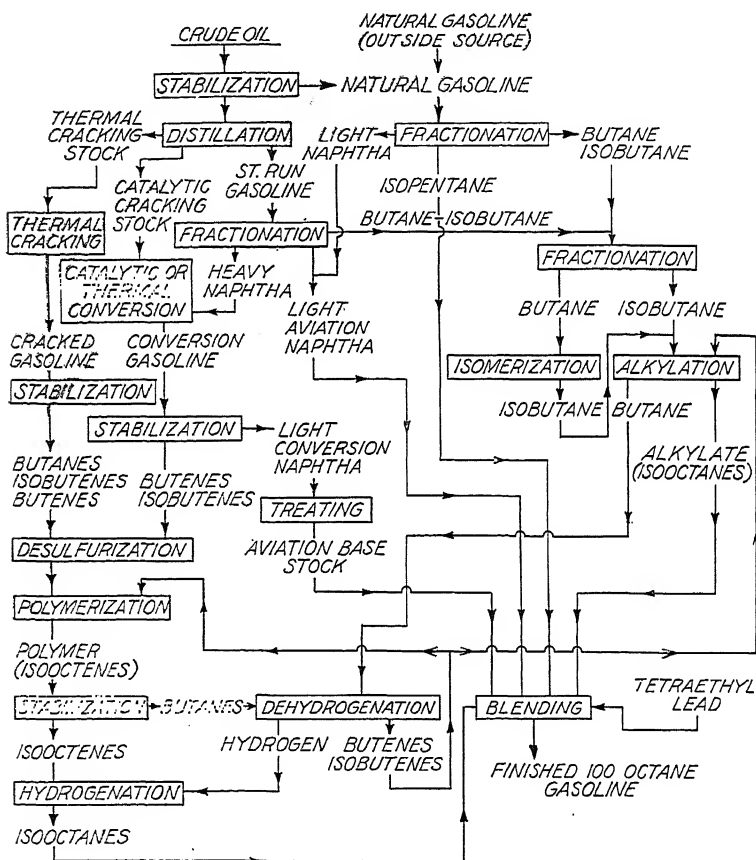
Fig. 8-VII.—Production of 100 octane aviation gasoline from straight-run and conversion naphthas and hydrogenated polymer and alkylate.

high-octane hydrocarbon manufacture and the utilization of two types of base stocks. Some refiners combine all processes shown and some only part of these. For simplification purposes only the products that contribute to the manufacture of aviation fuel are indicated on the diagrams.

FACTORS INFLUENCING THE BLENDING OF AVIATION GASOLINES

Since aviation gasolines are blends of various materials, it is obvious that the characteristics of the individual components have important effects on the blends themselves. The principal qualities which influence the character of the finished blend and which define the quantities of the individual components included are, in general, the following:

1. Antiknock qualities
    a. Octane number
    b. Blending octane number
    c. Lead susceptibility
2. Freezing point
3. Gum-forming tendencies
4. Sulfur content
5. Thermal properties
6. Volatility characteristics
    a. Boiling range
    b. Vapor pressure

These properties are those which in most cases are strictly controlled by specifications on the finished aviation gasoline. On the following pages the influence of these properties is discussed from the standpoint of the individual components contained in the various grades of aviation gasolines according to present manufacturing procedures.

Antiknock Qualities.—The characteristic of greatest importance in an aviation fuel is that of resistance to knocking or detonation, and the greatest advances in the technology of aviation gasoline have been directly due to the recognition of this property and the development of methods of evaluating it. The search for and discovery of knock suppressors such as tetraethyl lead and iron carbonyl, and high-antiknock hydrocarbons such as isooctane, neohexane, and more recently, triptane and cumene, were all the result of the effort to produce fuels of higher antiknock quality. In producing aviation gasolines having this property the qualities of the blending materials should be considered from the three principal standpoints of octane number, blending octane number, and tetraethyl lead susceptibility.

Octane Number.—Octane numbers of the individual components of aviation-fuel blends are valuable in most instances

in estimating only the approximate octane number of the finished gasoline. This is particularly true of hydrocarbons other than the paraffin type since the antiknock values of most classes of hydrocarbons are not quantitatively indicative of their octane numbers when blended with materials of a different type. With the saturated paraffins, however, the behavior of the different members in regard to knocking tendency when blended may be predicted with some degree of accuracy from their individual octane numbers.

The octane numbers of various materials used in blending the present-day aviation gasoline are found in Table 6-VII.

TABLE 6-VII.—OCTANE NUMBERS OF AVIATION GASOLINE BLENDING MATERIALS

Material	Octane Number*
Straight-run naphtha	65–80
Depentanized natural gasoline	65–75
Conversion naphtha	76–82
Alkylates	75–88
Hydrogenated polymers	80–90
Isooctane fractions	90–98
Isooctane (pure)	100
Neohexane fraction	90–95
Neohexane (pure)	94
Benzene	108
Cumene	110
Isopentane	90–95

* A.S.T.M.-C.F.R. Motor method. These octane numbers (taken from the literature) were determined by the A.S.T.M.-C.F.R. Motor method and as a result are not entirely comparable to the values that would be given by the A.S.T.M.-C.F.R. Aviation method, which is the one more commonly used for rating the finished aviation gasolines. However, for purposes of comparison, they indicate the relative antiknock values for the different stocks.

In blending finished aviation gasolines, particularly those of 91 or 100 octane number, the base stock should be of the highest possible antiknock value available to the individual refiner. In general, the higher the octane number of the base stock, the lesser will be the amount of high-octane hydrocarbons and/or tetraethyl lead necessary. Likewise, the higher the octane number of the high-octane blending agents, such as neohexane and isooctane, the lesser will be the amount of these required in the blend, all other things being equal.

The amount of heavier ends in straight-run gasoline affect the octane number considerably since the higher boiling straight-

chain paraffins have greatly decreased octane numbers.   This is shown[6] by the octane value of the following Mid-Continent naphthas of different end points:

End Point, °F.	Octane Number (A.S.T.M.-C.F.R. Motor)
300	74
350	70
400	67
437	64

Blending Octane Number.—In many cases, when two or more hydrocarbon compounds are blended and the octane number of the blend determined, it is found that their apparent octane values have changed and that of the blend is higher or lower than would be expected from the amounts blended and the octane numbers of the unblended compounds.   For example, diisobutene having an octane number of 87, when blended 50:50 with heptane having an octane number of 0, gives a blend having an octane number of 72 instead of 42 to 43 as would be expected. This behavior has resulted in the recognition of the antiknock characteristic of "blending octane number."*   The blending value of each compound is characteristic but not an exact number since it varies with the concentration and the characteristics of the other components in the blend.

Garner *et al.*[7] concluded that, in general, in blends of 25 per cent or less (1) the blending octane numbers of aromatic hydrocarbons are lower than the octane numbers of the pure hydrocarbons; (2) those of the olefins are higher; (3) those of the paraffins are approximately the same; and (4) those of the naphthenes are irregular and may be higher or lower.

Another characteristic of the blending octane numbers of hydrocarbons when added to gasoline blending stocks is that the blending octane number becomes higher the lower the octane number of the base gasoline.   Therefore, it is easier to raise the octane number of a gasoline of 50 octane number to 60 than to raise one of 60 to 70 by the addition of a high-antiknock-value hydrocarbon.

Although no definite statement can be made on the blending octane numbers of the various components used in present-day aviation gasoline unless the amounts and identity of the

* See discussion on pp. 64 and 65, Chap. IV.

constituents are defined, the following trends are generally characteristic:

1. The blending octane values of the straight-run and natural gasolines from paraffin and mixed base crudes are approximately the same as their unblended octane numbers.

2. The blending octane values of straight-run and natural gasolines from naphthenic or asphaltic base crudes may be lower or higher than their unblended octane numbers.

3. The blending values of the conversion naphthas are somewhat higher than the unblended octane numbers. This varies with the principal type of hydrocarbons contained in the naphtha. With a high paraffin content the blending values are comparable to the unblended octane numbers; with a high percentage of aromatics the values are usually higher. (This depends upon the type of aromatics. Branched-chain alkylated benzenes have much higher blending octane numbers than the straight-chain type.)

4. The blending values of the relatively pure isohydrocarbons used as high-octane blending agents are comparable to those of the unblended mixtures and in some instances are higher.

5. The blending values of the benzenes having saturated branched side chains are higher than their unblended octane numbers.

Tetraethyl Lead Susceptibility.—An important factor influencing the production of aviation gasolines of high-antiknock value under present practice is that of tetraethyl lead susceptibility of the blending components and of the blends themselves. The lead susceptibility is defined as the increase in antiknock value imparted to a hydrocarbon compound or mixture of compounds by the addition of definite amounts of tetraethyl lead fluid.[*,8] The lead response of a compound or mixture of compounds varies with each increment of lead added, with the individual character of the compound or mixture, and with the octane number of the unleaded material. A 90 octane number gasoline raised

* Composition of tetraethyl lead fluid (or "ethyl" fluid), 1-T:

	Per Cent
Lead tetraethyl	61.42
Ethylene dibromide	35.68
Kerosene and impurities	2.65
Dye	0.25

to 100 octane number by the addition of 1 cc. of tetraethyl lead is said to have a good lead susceptibility while one raised from 50 to 60 does not not because the increase of the antiknock value of the higher octane number stock represents a much greater effect in terms of engine operation.

In order to secure a straight-line relationship between lead response and octane number so that characteristic and com-
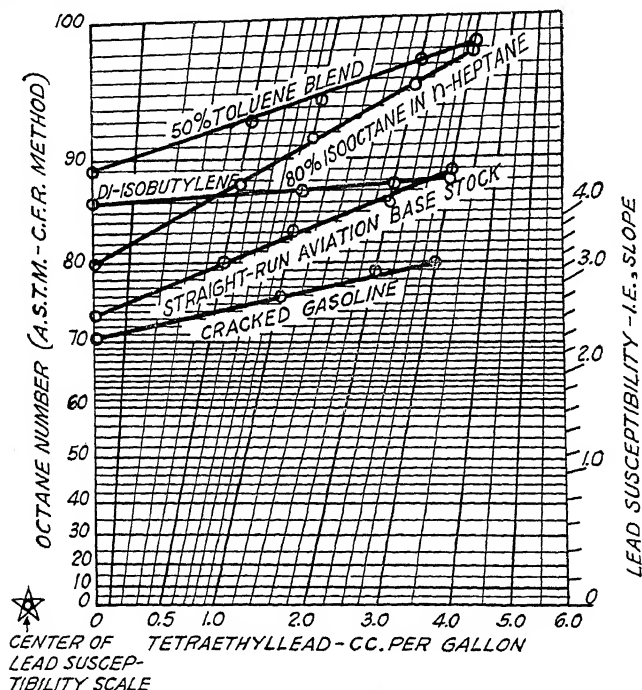
FIG. 9-VII.—Lead susceptibility chart for gasolines below 100 octane number
(*Courtesy of Ind. Eng. Chem.*)

parable values could be determined for all types of stocks, Hebl, Rendel, and Garton[9,10] devised an empirical chart for this purpose. A chart of this type is shown in Fig. 9-VII. By comparing the slopes (or lead susceptibilities) of various stocks plotted on these coordinates, it is shown that for the same lead susceptibility the octane number increase for a given amount of lead is much higher for the lower antiknock value stocks.

Since many of the materials composing 100 octane aviation gasoline have octane numbers above 100 and since the gasolines

themselves are tending toward higher octane numbers, an extension of the octane scale above 100 was found necessary. Cattaneo and Stanley[11] effected this extension by increasing the
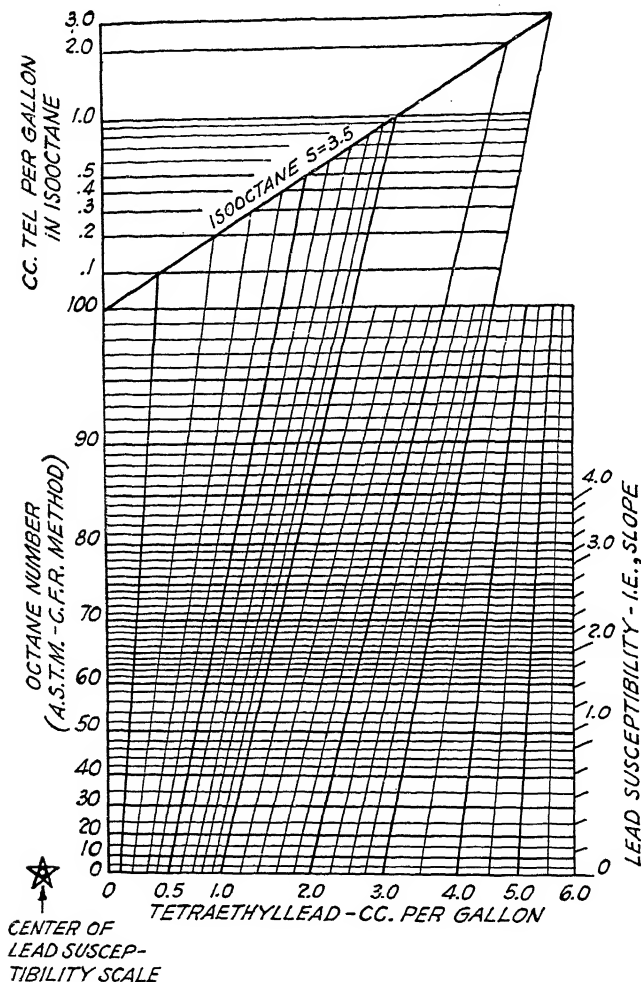
FIG. 10-VII.—Lead susceptibility chart for gasolines extended above 100 octane number. (*Courtesy of Ind. Eng. Chem.*)

range of the lead susceptibility chart of Hebl *et al.*, as is shown in Fig. 10-VII. The octane scale is used up to 100 octane number and isooctane plus milliliters (or cubic centimeters) of tetraethyl lead for antiknock values above 100.

Table 7-VII lists typical lead susceptibilities of various blending components used in aviation gasoline.

TABLE 7-VII.—LEAD SUSCEPTIBILITIES OF AVIATION GASOLINE BLENDING COMPONENTS

(A.S.T.M.-C.F.R. Motor method octane number)

	Tetraethyl lead, cc./gal.						
	0.0	1.0	2.0	3.0	4.0	5.0	6.0
Aviation base stocks:							
Natural gasoline—Mid-Continent...........	65	74	78	80	82		
Natural gasoline—East Texas...............	70	78	83	88	91	92	93
Straight-run naphtha—Mid-Continent.......	65	73	....	79	81		
Straight-run naphtha—California............	70	79	83	85			
Conversion naphtha—Houdry.............	77–78	....	....	91–93			
Conversion naphtha—Reversion............	77–82	84–87	88–89	90–90			
Conversion naphtha—T.C.C...............	77–80	....	....	92–95	94–97		
Conversion naphtha—Hydroforming........	75–80	84	86	87			
High-octane hydrocarbons:							
Alkylates..............	92	+0.1*	+0.3*	+0.4*	+0.5*		
Hydrogenated polymers (selective)...........	92–94	103–106	107–109	110–112	113–115		
Isooctane..............	100	109	112	114	118		
Neohexane.............	94	107	112	114	117		
Isopentane.............	90	99†	103†	105†			

* Matches isooctane plus * cc.T.E.L. per gal.
† Estimated from blend data.

Various investigations of the lead susceptibilities of individual members of the different hydrocarbon types have shown that some evidence a greater antiknock value increase for a given quantity of tetraethyl lead than others. The hydrocarbon types having the greatest tendency to knock (or having the lowest octane number) show the greatest response to lead. The order of the different hydrocarbon types in regard to decreasing lead susceptibility is listed as follows:[12]

1. Paraffins.
2. Naphthenes.
3. Aromatics with saturated side chains.
4. Olefins and diolefins.
5. Unsaturated cyclic compounds.

The lead susceptibilities of gasolines and gasoline blends depend upon two principal factors: (1) the initial antiknock value of the gasoline before leading and (2) the hydrocarbon types contained in the blend. In general, those gasolines having lower antiknock values have greater response to tetraethyl lead additions than those of higher octane number. In regard to hydrocarbon content, the gasolines containing paraffins and isoparaffins such as the straight-run type have much greater lead susceptibility than those high in olefins such as the thermal cracked gasolines and polymer gasolines from nonselective polymerization. The conversion naphthas from catalytic cracking and reforming generally have lower lead susceptibilities than the straight-run naphthas because they are of higher initial octane number and contain a higher percentage of aromatics.

The lead response of a finished aviation gasoline ready for leading depends mainly upon the type and quantity of the various blending components used. The amount of lead necessary to achieve a specified octane number must be determined by test, since prediction of the amount from the lead susceptibilities of the components is extremely difficult.

TABLE 8-VII.—LEAD SUSCEPTIBILITIES OF VARIOUS AVIATION GASOLINE BLENDS[13]

(Octane Number—A.S.T.M.-C.F.R. Motor method)

Blend	cc. T.E.L./gal.				
	0	1.0	2.0	3.0	4.0
Straight-run 70 octane number: isopentane, 90 octane number :: 50:50	80	87	91	94	95
Straight-run 70 octane number: isooctane, 100 octane number :: 50:50	84	90	94	97	99
Straight-run 70 octane number: benzene, 100+ octane number :: 50:50	81	85	88	90	91
Straight-run 70 octane number: ethyl benzene, 96 octane number :: 50:50	85	89	92	93	94

Some lead susceptibilities of aviation-fuel blends are shown in Table 8-VII.

Effect of Impurities on Lead Susceptibility.—The lead susceptibilities of the gasoline blends and the hydrocarbon mixtures are adversely affected to a great extent by the sulfur and sulfur compounds. This effect is apparently due to the sulfur reacting with the lead, forming lead sulfide, which is of no value as an antidetonating agent. The effect is not so marked in aviation gasolines as it is in motor gasolines because the maximum permissible sulfur content is much lower in the former type of fuel.

That it is of significant importance, however, can be seen from Table 9-VII which shows the effect of sulfur content on the lead response of a Borger, Texas, natural gasoline containing small amounts of sulfur.

TABLE 9-VII.—LEAD RESPONSE AND SULFUR CONTENT OF NATURAL
GASOLINE[14]

(Octane number-Motor method)

	Sulfur, %			
	0.037	0.008	0.004	0.002
Clear.............................	67.2	69.5	69.6	69.7
1 cc. tetraethyl lead...............	75.6	80.0	81.0	81.4
3 cc. tetraethyl lead...............	82.1	85.3	86.8	87.5
6 cc. tetraethyl lead...............	86.6	91.2	92.8	93.2

The data indicate that even in the low-sulfur-content range shown, the difference in lead susceptibility for a gasoline of 0.037 per cent sulfur content as against 0.008 per cent is approximately five octane units. Thus, the importance of desulfurization of the components of aviation gasolines to a minimum sulfur content is clearly evident.

A method of calculating the decrease in lead susceptibility due to different types of sulfur compounds has been presented by Ryan.[15] This method requires a quantitative sulfur-type analysis.

Freezing Point.—The freezing point of all present-day aviation gasolines is specified at −76°F. max., and it is determined by the temperature at which one or more of the compounds contained begin to crystallize. This problem is of no great importance in most cases since the types of blends do not contain

materials of high freezing point.   Benzene blends are exceptional because the high freezing point of that compound (42°F.) limits the maximum amount permissible to around 15 per cent.   Bass[16] states that maximum amount of benzene allowable to meet a −60°F. freezing point in the aviation gasoline to which it is added is 20 per cent.   It is evident that the hydrocarbon type of other stocks contained in the gasoline would have some effect on the amount of benzene possible to use.   The substituted aromatics used as blending agents have lower freezing points and offer no problem in this respect.

Gum and Oxidation Stability.—The gum stability or resistance to oxidation of an aviation gasoline is an important requirement which is closely controlled by laboratory test methods (see Chap. III) which are somewhat questionable in regard to their ability to indicate the true performance of the fuel.   The stability of the gasoline is dependent upon the types of hydrocarbons contained.   The straight-run base stocks and the high-octane hydrocarbon blending materials are composed of paraffinic or aromatic types and as a result are highly resistant to oxidation and give no difficulty in regard to gum formation.   The conversion naphthas used as base blending stocks may contain olefinic constituents since they are produced in most cases under conditions favoring some olefin formation.   If the unblended stock does not pass the gum and stability tests, it will be usually unsatisfactory in the aviation fuel.   In most cases the olefin content is lowered or entirely removed by suitable treatment with clay or acid.

The addition of certain gum inhibitors to all grades of aviation gasoline is permitted and the amount is not to exceed 1 lb. per 5,000 gal.   The presence of these inhibitors permits the use of a somewhat more unstable base stock or blending components but still does not permit the use of thermal cracked gasolines or straight polymers because of their high degree of unsaturation.

The permissible gum inhibitors are

Monobenzyl-p-aminophenol.

Isobutyl-p-aminophenol.

n-Butyl-p-aminophenol.

n,n'-Dibutyl-p-aminophenol.

o-, m-, and p-cresols.

α-naphthol.

These substances when added in small amounts to gasolines prevent, for a time, oxidation and gum formation by inhibiting the reaction between the oxygen of the air with the hydrocarbon constitutents.   After the inhibitor is exhausted by being oxidized itself, the gum formation proceeds at a rapid rate, apparently accelerated by the reaction products of the inhibitor.

Sulfur Content.—The sulfur content of all grades of aviation gasoline is limited to 0.05 per cent maximum by specification, and all components going into the finished blend should contain no more than this amount and preferably less.   Usually the high-octane blending components, with the exception of perhaps benzene, are by virtue of their conversion process source naturally low in sulfur content.   The base stocks, particularly the straight-run type and certain of the conversion types, may require desulfurization before being used in aviation gasoline.

The principal detrimental effects of sulfur and sulfur compounds are as follows:

1. Their presence causes a lowering of the octane number of the blend.

2. They cause a definite loss in lead susceptibility.

3. They may, depending upon their type, tend to accelerate oxidation and gumming reactions.

4. They may cause corrosion either in the fuel or exhaust system.

Thermal Qualities.—The thermal properties of aviation gasoline of primary interest are the heats of combustion and heats of vaporization.   The specifications eliminate gasolines having heats of combustion lower than 18,300 B.t.u. per lb. for the 73 octane grade and 18,700 B.t.u. per lb. for the 91 and 100 octane grades.   There is no specification for the heat of vaporization and, although it is known that a high latent heat for a given heat input will reduce cylinder and piston temperatures if no undesirable combustion characteristics take place,[17] this characteristic is not obtainable from the normal hydrocarbon-type gasolines.

In regard to combustion value, there is no problem involved with the usual paraffinic types of aviation gasolines since the heats of combustion of the constituents are all sufficiently high to enable the blend to meet the specifications.   In the case of the aromatics, however, particularly benzene and the methyl

substituted benzenes, the heats of combustion are lower and the amounts possible to blend with the paraffinic type hydrocarbons are therefore limited. Table 10-VII lists some of the blending components of aviation gasoline and other compounds, together with their heats of combustion and heats of vaporization.

TABLE 10-VII.—THERMAL PROPERTIES OF AVIATION GASOLINE BLENDING COMPONENTS[17]

Component	Heat of combustion (gross) B.t.u./lb.	Latent heat, B.t.u./lb., approx.
Straight-run gasoline	20,000–20,600	140–150
Conversion gasoline	20,000–20,600	140–150
Alkylates (isooctanes)	20,500	140
Isooctane	20,500	140
Triptane, 2,2,3-trimethyl butane	20,600	140
Neohexane	20,700	150
Isopentane	20,800	160
Benzene	18,000	170
Toluene	18,300	160
Xylenes	18,500	150
Diisopropyl ether	16,900	123
Methanol	9,500	473
Ethanol	12,700	368
Isopropanol	14,400	287
Acetone	13,100	223
Cyclohexane	20,100	160

Boiling Range.—The boiling range of an aviation gasoline is important since the volume percentage boiling points have a marked influence on the operating efficiency of aircraft engines. The 10 per cent point, which is limited by specification to 158°F., determines the ease of starting, vapor-locking tendency, distribution in the manifold, and carburetor icing tendencies. The 50 per cent point, specified at a maximum of 212°F., affects fuel distribution, warm-up time, and throttle response. The 90 per cent point, specified at 257°F., is of less significance but determines somewhat the power output and fuel economy in flight. The minimum limits are controlled by a specification of 307°F. for the 10 + 50 per cent points.

Table 11-VII gives the boiling points or boiling ranges for the various stocks that are to be found in present-day aviation gasoline.

By comparing the specifications established for the finished aviation gasolines with the boiling ranges of the materials in

TABLE 11-VII.—BOILING RANGES OF AVIATION GASOLINE COMPONENTS

Blending Materials	Approx. Boiling Point or Range, °F.
Isopentane	82
Neohexane	122
Neohexane fraction	110–150
Isooctane (pure)	202
Isooctane fraction	190–230
Benzene	176
Cumene	152
Depentanized natural gasoline	100–250
Straight-run aviation naphtha	100–300
Conversion naphtha	100–330
Alkylate fraction	190–250
Hydrogenated mixed polymer fraction	160–250

Table 11-VII, we readily see that the pure hydrocarbons or hydrocarbon mixtures unblended would not fulfill the necessary requirements because of their narrow boiling ranges. In considering boiling point alone, neohexane, for example, boils much lower than the 10 per cent specification, isooctane between the specified 10 and 50 per cent points, and the other mixtures, with the exception of the base stocks, boil at temperatures extending over portions of the required range. Based upon true-boiling-point distillations, the actual boiling temperatures of the various blending materials show up as flat steps on the curve. The effect of the boiling point of any pure substance would be pronounced under this condition and the amount utilized in the blend in relation to the amounts of other components and their respective boiling points would be more definitely limited than is actually the case. The A.S.T.M. distillation, which is essentially a nonfractionating method, greatly reduces the effect of large quantities of a substance boiling at one temperature. Consequently the distillation curve is somewhat smoothed out.

Thus, substances having narrow boiling ranges, or single boiling points, may be used in larger proportion than would be indicated from their boiling temperatures and still allow the blend to fulfill the specifications. There are certain limits to the amounts of such materials that can be blended and the limits have to be determined experimentally. These are determined on blends in which the proportion of the components is varied within the usable ranges and the A.S.T.M. distillations determined.

The distillation curve for a suitable aviation gasoline should be a straight line over the greater portion of its range.   Medium volatility is better than either high or low volatility since the highly volatile fuels give poorer fuel economy and power characteristics while the low volatility fuels tend to give poorer starting characteristics, fuel distribution, and throttle response.

Vapor Pressure.—The vapor pressure of all grades of aviation fuel is limited by specification to 7.0 lb., Reid.   This specification in conjunction with the volatility requirements controls the amount of low vapor pressure material that can be contained in the blends.   Table 12-VII lists the vapor pressures of the base stocks and high-octane hydrocarbon components which may be included in the various grades of aviation gasoline.

TABLE 12-VII.—VAPOR PRESSURES OF AVIATION GASOLINE COMPONENTS

Blending Component	Reid Vapor Pressure, lb.
Isopentane	21
Neohexane	5.9
Isooctane	1.5
Benzene	3.2
Cumene	1−
Straight-run aviation naphtha*	2–5
Conversion naphtha*	2–7
Alkylate*	2–3
Hydropolymer*	2–3

* The vapor pressures of these stocks depend entirely upon their degree of fractionation or stabilization.

The data given in Table 12-VII indicate that from the standpoint of the maximum vapor pressure permitted in the finished gasoline, all the materials listed with the exception of isopentane could be utilized as aviation gasolines.   The maximum isopentane content of the fuel blend is limited because of its relatively high vapor pressure of 21 lb., and the amount of this material that it is possible to blend with the other components constituting the aviation gasoline is determined mainly by the amounts of other materials included and their combined vapor pressure before the addition of isopentane.   For example, a conventional 100 octane aviation gasoline containing straight-run naphtha and alkylate or isooctane mixture can contain normally only 10 to 15 per cent of isopentane without exceed the 7-lb. vapor pressure specification.   With a conversion naphtha stabilized to 5-lb. vapor pressure used as a base stock and neohexane as a high-

octane blending agent, the amount of isopentane possible to include is limited to a much lower percentage. In many cases, it is possible to blend a finished aviation gasoline without the inclusion of any isopentane, and the vapor pressure in such a blend is achieved by the stabilization of the base stock to the amount required. This practice is not usual in the 100 octane grade where usually the amounts of isopentane utilized range from 10 to 15 per cent. In the 91 and 73 octane grades, the vapor pressure is usually imparted by the correctly stabilized base stock rather than by the addition of high vapor pressure constituents.

For a given refining procedure used in the production of a standard type of gasoline, the prediction of the approximate vapor pressure of the blend based on the type and quantity of components is based upon charts that are drawn from experimental data. Approximate vapor pressures of blends may be calculated[18] from the Reid vapor pressures of the components and their mol per cents, using Dalton's law of partial pressures. (If true vapor pressures are used, the vapor pressure of the blend may be determined accurately by this method.)

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CHAPTER VIII

SPECIAL AVIATION FUELS AND AVIATION-FUEL COMPONENTS

In the preceding chapters the properties, tests, and manufacturing methods for the production of the conventional type of aviation gasolines have been discussed. From the standpoint of present-day practices and indicated future trends, this type of aviation gasoline occupies a dominant position in relation to that of other light fuels used for aviation purposes, and, based on its volume of production and use, it may be considered the only type worthy of consideration. However, there have been and are used at present to some extent special aviation fuels and blending components which may be placed in the general classification of aviation gasolines (not including other fuels such as diesel fuels), but which do not fulfill all the requirements of present-day aviation gasoline. This chapter is devoted to the consideration of these materials.

The blending components that have been investigated and used in aviation gasoline to some extent are the aliphatic ethers, ketones, and alcohols. The members of each group that have been used because of certain valuable properties are listed as follows:

1. Ethers
    a. Diisopropyl ether
    b. *tert* Butyl ethyl ether
    c. Various higher branched-chain ethers
2. Ketones
    a. Acetone
    b. Methyl ethyl ketone
3. Alcohols
    a. Methanol
    b. Ethanol
    c. Isopropanol
    d. *tert*-Butanol

The special fuels to be considered are those of the regular aviation gasoline type containing the foregoing components

singly or in combination, and high-flash or "safety" aviation fuels which are a definite class of gasolines of low volatility with antiknock characteristics comparable to those of the regular fuels.

SPECIAL BLENDING COMPONENTS—ETHERS

For a number of years after the search for high-antiknock blending components had begun, all ethers were considered to have pro-knocking characteristics. This conclusion was based on the observation that the addition of ethyl ether increased the knocking tendency of a gasoline fuel. However, Buc and Aldrin[1] in 1936 in a paper discussing the properties of diisopropyl ether showed that it had a high-octane number (98 to 99, Army Method), a high blending octane value, and a high lead response in blends of the aviation-gasoline type. Since that time, other ethers have been studied on the basis of use as blending components in aviation gasoline and have been found to have acceptable antiknock characteristics.[2]

Manufacture and Properties.—Diisopropyl ether is probably the most prominent compound of the ether types in relation to their use in the production of high-octane aviation fuels. This compound is produced by the sulfation of propene, forming isopropyl sulfate; the hydration of the sulfate, forming isopropyl alcohol; and the dehydration of the alcohol, forming diisopropyl ether. The reaction steps are as follows:

$$
\begin{array}{cc}
\text{H H H} & \text{H H H} \\
\text{HC}=\text{C}-\text{CH} + \text{H}_2\text{SO}_4 \cdot \quad \cdot \text{HC}-\text{C}-\text{CH} & \quad (1) \\
\quad\quad\text{H} & \text{H }|\text{ H} \\
& \text{HSO}_4
\end{array}
$$

<div align="center">Propene   Isopropyl sulfate</div>

$$
\begin{array}{cc}
\text{H H H} & \text{H H H} \\
\text{HC}-\text{C}-\text{CH} + \text{H}_2\text{O} \rightarrow \text{HC}-\text{C}-\text{CH} + \text{H}_2\text{SO}_4 & \quad (2) \\
\text{H }|\text{ H} & \text{H }|\text{ H} \\
\text{HSO}_4 & \text{OH}
\end{array}
$$

<div align="center">Isopropyl sulfate   Isopropyl alcohol</div>

$$
\begin{array}{cc}
 & \text{H}\quad\quad\text{H} \\
 & \text{HCH HCH} \\
\text{H H H} & \quad|\quad\quad| \\
2 \cdot \text{HC}-\text{C}-\text{CH} + \text{H}_2\text{SO}_4 \rightarrow \text{HC}-\text{O}-\text{CH} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \quad (3) \\
\text{H }|\text{ H} & \quad|\quad\quad| \\
\quad\text{OH} & \text{HCH HCH} \\
 & \text{H}\quad\quad\text{H}
\end{array}
$$

<div align="center">Isopropyl alcohol   Diisopropyl ether</div>
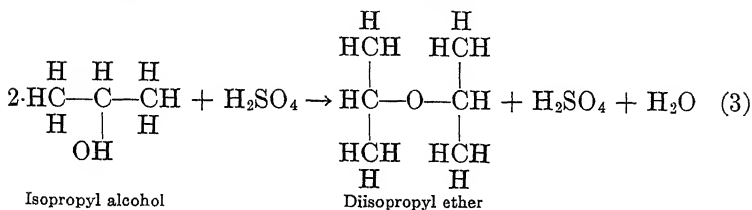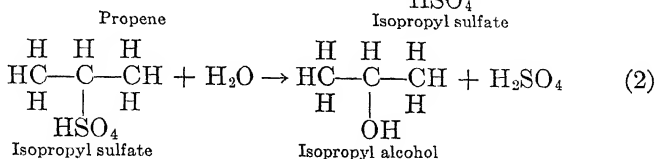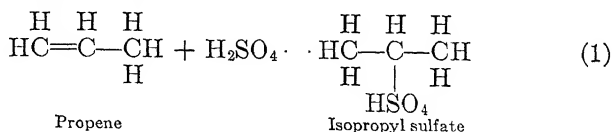
An alternative method, wherein the isopropyl sulfate is reacted with isopropyl alcohol to form diisopropyl ether and sulfuric acid, is shown as follows:

$$
\begin{array}{ccc}
& & \overset{\displaystyle H}{\underset{\displaystyle}{HCH}} \quad \overset{\displaystyle H}{\underset{\displaystyle}{HCH}} \\
\overset{\displaystyle H\ H\ H}{HC{-}C{-}CH} + \overset{\displaystyle H\ H\ H}{HC{-}C{-}CH} \rightarrow \overset{}{HC{-}O{-}CH} + H_2SO_4 \\
\underset{\displaystyle HSO_4}{H\ |\ H} \qquad \underset{\displaystyle OH}{H\ |\ H} \qquad \underset{\displaystyle \overset{HCH}{H}}{} \; \underset{\displaystyle \overset{HCH}{H}}{}
\end{array}
$$

Isopropyl sulfate   Isopropyl alcohol   Diisopropyl ether
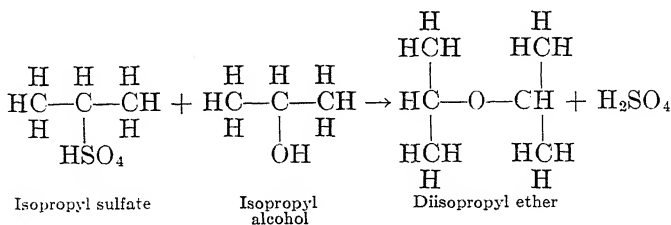
Mixed ethers may be made in a similar manner by reacting, for example, ethyl sulfate with *tert*-butanol or *tert*-butyl sulfate with ethanol to form *tert*-butyl ethyl ether.   The sulfates and alcohols may be made from olefinic petroleum gases by reacting them with sulfuric acid to form the sulfates and hydrating the sulfates to form the corresponding alcohols.

There is a strong tendency for polymerization of the olefins in the presence of sulfuric acid, and this tendency must be retarded in order to obtain reasonable yields.   Propene polymerization in the presence of sulfuric acid is retarded[3] (1) by keeping the mixture relatively cool and using 85 per cent strength acid, (2) by conducting the reaction in the presence of an inert oil, (3) by maintaining a high partial pressure of propene, or (4) by using a weaker acid at elevated temperatures and pressures.

TABLE 1-VIII.—PROPERTIES OF ETHERS SUITABLE FOR AVIATION GASOLINE BLENDS

	Diisopropyl ether[1]	*tert*-Butyl ethyl ether[4]
Boiling point, °F	153–158	155
Calorific value net, B.t.u./lb	15,600	15,600
Calorific value gross, B.t.u./lb	16,900	16,900
Density at 68°F	0.725	0.74 at 60°F.
Freezing point, °F	−125	
Heat of vaporization, B.t.u./lb	123	
Octane number (A.S.T.M. Motor)	98	100 + 0.1 cc.
Vapor pressure, Reid	5.3	
Water solubility, %	0.65 at 77°F.	

The properties of two of the ethers in which we are interested from the standpoint of aviation gasoline manufacture are listed in Table 1-VIII.

In all respects except calorific value the ethers shown above are suitable for blending with aviation-fuel stocks. The low heats of combustion are a definite disadvantage.

Properties of Aviation Gasoline—Ether Blends.—There is little published data on the use of the different ethers as blending components in aviation gasoline. Buc and Aldrin discussed the use of diisopropyl ether and claimed that in many respects this compound was comparable to or even better than isooctane as a high-octane blending material although in some respects it was inferior.

In regard to the characteristics in the presence of water of blends containing diisopropyl ether,[1] it was found that 1.5 per cent of the ether contained was extracted by shaking with water (50:50). The amount of water dissolved at 77°F. by an aviation gasoline containing 40 per cent of diisopropyl ether was found to be 0.085 per cent as compared to 0.007 per cent dissolved by regular aviation gasoline, and the amount settled out at −20°F. was 0.005 ml. per 100 ml. of gasoline-ether blend compared to 0.0005 ml. per 100 ml. of regular aviation gasoline blend. Although the tolerance of these blends for water is greater than that of the regular aviation gasoline, it is claimed that the quantities involved do not prohibit their use under most conditions.

Buc and Aldrin have shown that stability in storage and oxidation tests, run on the ether blends containing 1.4 mg. of

TABLE 2-VIII.—ANTIKNOCK VALUES OF DIISOPROPYL ETHER AND
ISOOCTANE BLENDS (A.S.T.M.)
(Motor Octane Numbers)

Blending agent, %	Diisopropyl ether, cc. T.E.L./gal.			Isooctane (crude), cc. T.E.L./gal.		
	0.0	1.0	3.0	0.0	1.0	3.0
0	73.5	82.0	87.5	73.5	82.0	87.5
10	76.3	84.1	89.3	76.0	84.0	89.0
25	80.5	88.6	94.0	79.4	86.8	91.4
40	85.0	....	97.5	83.0	....	94.2

inhibitor (B.A.P.) per 100 ml. of gasoline, gave the following results: stable in storage at the end of $2\frac{1}{2}$ months; induction period exceeded 7 hr.; and gum contents by various methods, 1.0 to 4.5 mg. per 100 ml. These results indicated a satisfactory stability.

The blending octane values and lead susceptibilities of the diisopropyl ether blends compared to those of isooctane are shown in Table 2-VIII.

Table 2-VIII shows that the blending octane value and lead susceptibilities of the diisopropyl ether blends are slightly higher than those of the isooctane blends. Heron and Beatty[4] reported a slight to high lead response in blends for other branched-chain ethers.

The principal disadvantage of this type of blend lies in its comparatively low heat content (heat of combustion). On a weight basis the heat content of diisopropyl ether is 18 per cent less than that of isooctane.

Performance of Aviation Gasoline—Ether Blends.—Tests on multicylinder engines using diisopropyl ether blends indicate

1. Blends of this type show freedom from carburetor icing.

2. The 100 octane number ether blend has a minimum specific fuel consumption 13 per cent lower than 92 octane number regular gasoline under cruising conditions.

3. The 100 octane number ether blend has a minimum specific fuel consumption 5 to 7 per cent higher than 100 octane number regular aviation fuel under cruising conditions.

4. Both 100 octane number blends are equal in power output and consumption characteristics under take-off and climbing conditions.

Little information has been published on the properties and performance of the higher branched-chain ether blends, but it may reasonably be assumed from what few data are offered that both the properties and the performance characteristics would be somewhat similar to those of the diisopropyl ether blends.

SPECIAL BLENDING COMPONENTS—KETONES

Acetone and methyl ethyl ketone have been found to have high-antiknock values and good lead susceptibilities when blended with aviation base stock. Their principal disadvantages are

their low heating values (as are those of all oxygen-containing compounds) and their water solubility characteristics.

Manufacture and Properties.—Acetone may be produced by several methods: (1) by fermentation of corn and molasses, (2) catalytically from ethanol, and (3) by catalytic dehydrogenation of isopropanol. The last two methods are of most interest to petroleum refiners since the alcohols may be produced from the olefin gases, ethene and propene.

Acetone is produced[5] from ethanol by passing ethanol and steam over catalysts composed of oxides of iron, manganese, or copper, promoted by oxides of calcium or magnesium (or at low pressures by the oxides of nickel cobalt or chromium), at 932°F. It is also produced from isopropanol by passing the alcohol over metal oxide catalysts in the presence of small amounts of air at high temperatures.

Methyl ethyl ketone may be produced from the catalytic dehydrogenation of butanol-2 which can be made from butene-2 (found in refinery cracking gases) by passing the alcohol over catalysts composed of metal alloys of copper and zinc or zinc chromate, and sodium carbonate at temperatures of 650 to 900°F.

Properties of the ketones that have been investigated as aviation-fuel blending agents are found in Table 3-VIII.

TABLE 3-VIII.—PROPERTIES OF KETONES

	Acetone	Methyl ethyl ketone
Boiling point, °F	133	175
Calorific value, gross, B.t.u./lb	13,100	14,500
Density at 60°F	0.796	0.810
Freezing point, °F	−138	−124
Heat of vaporization, B.t.u./lb	223	
Octane number (A.S.T.M. Motor)	100	100
Vapor pressure, Reid, lb	7.6	3.2
Water solubility	Miscible	Soluble

The calorific values of these ketones are much lower than those of the corresponding ethers, and on a weight basis are 29 to 36 per cent lower than that of isooctane.[6] In addition, acetone is completely miscible with water, and methyl ethyl ketone is very soluble. The lead susceptibility of acetone is said to be zero when it is unblended.[4]

Properties of Aviation Gasoline—Ketone Blends.—The octane numbers of the ketones are of the same order as that of isooctane and the blending octane numbers are slightly higher.   The lead susceptibilities of the ketone-gasoline blends are slightly lower than those of the isooctane-gasoline blends.   These trends are shown in Table 4-VIII.

TABLE 4-VIII.—LEAD SUSCEPTIBILITIES OF KETONE-GASOLINE BLENDS

	Octane number (A.S.T.M. Motor)		
	Acetone	Methyl ethyl ketone	Isooctane
Unblended.........................	100	99	100
50% blended with 70 octane:			
Number straight-run gasoline......	85	86	84
+1 cc. T.E.L./gal................	93	93	90
+2 cc. T.E.L./gal................	96	95	94
+3 cc. T.E.L./gal................	98	96	97
+4 cc. T.E.L./gal................	99	97	99

The aviation fuels containing ketones are unstable in the presence of water because of their high water solubility.   Blends containing acetone or methyl ethyl ketone in any appreciable percentage have lower heats of combustion than the regular gasolines. This results in a higher specific fuel consumption, particularly under lean mixture conditions in cruising operation. The water solubility of the ketones enables their fuel blends to have good deicing properties.

SPECIAL BLENDING COMPONENTS—ALCOHOLS

Alcohols have been used as blending agents in motor gasolines in Europe for a number of years.   There has been a great deal of agitation by certain groups in this country from time to time to legislate the compulsory use of ethanol as a blending component of motor gasoline; consequently, the subject of alcohol gasoline blends and their characteristics has resulted in a large amount of investigation.[7]

The alcohols that have been used as blending agents for aviation gasoline have certain advantages, namely, high-octane number and high latent heat of vaporization; and certain dis-

advantages such as low lead susceptibility, a tendency for the separation of the alcohol in presence of water, and a low heat of combustion.

In spite of their disadvantages, alcohol blends in general have certain qualities in regard to engine performance that have resulted, to a small extent, in their use for special purposes where their disadvantages are not the controlling factors.

The principal alcohols that have been investigated are methanol, ethanol, and isopropanol.

Manufacture and Properties.—Methanol is produced principally by three methods: (1) destructive distillation of wood, (2) high-pressure synthesis of water gas, and (3) catalytic oxidation of methane or natural gas. The first method is of minor importance compared to the cheaper synthetic processes.

Methanol is made from water gas[8] (carbon monoxide and hydrogen) at low temperatures and high pressures under the influence of catalysts. The reaction is shown as follows:

$$CO + 2H_2 \rightarrow CH_3OH$$
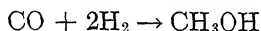
The catalysts consist of mixtures of metallic oxides such as zinc, copper, and chromium oxides or mixtures of metals, alloys, and oxides. The temperature conditions, depending upon the catalyst, range from 480 to 790°F. and pressures from 750 to 2,750 lb. per sq. in.

Methanol from methane or natural gas[9] may be produced by vapor phase oxidation by oxygen or air with or without the use of added catalysts. Temperatures range from 660 to 840°F. and pressures around 750 lb. per sq. in. The catalysts are vanadium pentoxide (and oxides of similar-type metals) and diethyl ether. In some cases inert gases such as nitrogen are added to the mixture of hydrocarbon gas and air for better control of the reaction. The reaction is idealized as follows:

$$\underset{\text{Methane}}{2CH_4} + O_2 \rightarrow \underset{\text{Methyl alcohol}}{2CH_3OH}$$
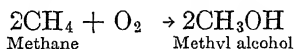
Ethanol is produced by fermentation of agricultural products or synthetically from cracked olefinic gases. In 1937 about 10 per cent of the ethanol produced in the United States was from cracked gases,[6] while in 1941 the quantity produced from this source amounted to about 23 per cent.[6a] The principal method[10] of production of ethanol from petroleum cracked gases

is that of absorption of ethene in sulfuric acid and hydration of the ethyl sulfate formed. Ninety-five per cent sulfuric acid is used in this process at temperatures up to 210°F. Catalysts, such as cuprous oxide and copper salts, have been used to increase the efficiency of ethene absorption. The temperature range for ethene absorption is 140 to 210°F. and the pressure range from 0 to 300 lb. per sq. in.

The reaction steps are as follows:

$$\underset{\text{Ethene}}{\overset{\text{H\quad H}}{HC\!\!=\!\!CH}} + H_2SO_4 \rightarrow \underset{\text{Ethyl sulfate}}{\overset{\text{H\quad H}}{\underset{\text{H\quad H}}{HC\!-\!C\!-\!SO_4H}}} \tag{1}$$

$$\underset{\substack{\text{H\quad H}\\ \text{Ethyl sulfate}}}{\overset{\text{H\quad H}}{HC\!-\!C\!-\!SO_4H}} + H_2O \rightarrow \underset{\substack{\text{H\quad H}\\ \text{Ethanol}}}{\overset{\text{H\quad H}}{HC\!-\!C\!-\!OH}} + H_2SO_4 \tag{2}$$
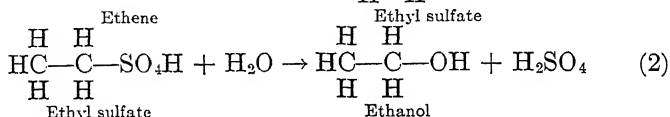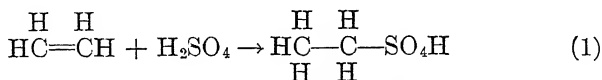
When the mixture is diluted with water to the stage where the concentration of the acid reaches 64 per cent, the separation of the alcohol takes place.

Various vapor phase methods[10] are employed for ethanol production which hydrate ethene with water at temperatures of 300 to 660°F. under pressures ranging from 15 to 1,500 lb. per sq. in. and under influence of catalysts such as sulfuric, phosphoric, tungstic acids, and caustic soda or potash.

Isopropanol and tertiary butanol are usually manufactured[11] by the sulfuric acid absorption of propene and isobutene from cracked gases, and hydrating the sulfates formed to the alcohols by diluting the acid containing the sulfates with water.

In isopropanol production sulfuric acid (80 to 85 per cent strength) is utilized at temperatures of 60 to 70°F. In *tert*-butanol production the strength of the acid is about 65 per cent and the temperatures 50 to 60°F.

The reactions in the formation of isopropanol are as follows:

$$\underset{\text{Propene}}{\overset{\text{H\quad H\quad H}}{\underset{\text{H}}{HC\!-\!C\!\!=\!\!CH}}} + H_2SO_4 \rightarrow \underset{\substack{\text{HSO}_4\\ \text{Isopropyl sulfate}}}{\overset{\text{H\quad H\quad H}}{\underset{\text{H}\quad|\quad\text{H}}{HC\!-\!C\!-\!CH}}} \tag{1}$$

$$\underset{\substack{\text{H}\quad|\quad\text{H}\\ \text{HSO}_4\\ \text{Isopropyl sulfate}}}{\overset{\text{H\quad H\quad H}}{HC\!-\!C\!-\!CH}} + H_2O \rightarrow \underset{\substack{\text{H}\quad|\quad\text{H}\\ \text{OH}\\ \text{Isopropanol}}}{\overset{\text{H\quad H\quad H}}{HC\!-\!C\!-\!CH}} + H_2SO_4 \tag{2}$$
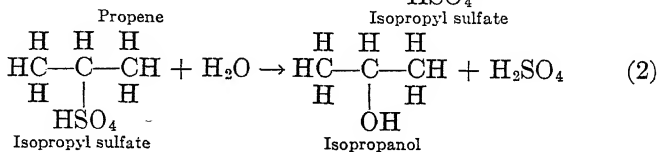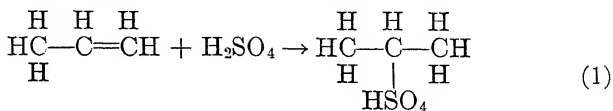
In the formation of tertiary butanol the reactions are

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{HC} & \text{HCH} \\
\text{H} \;\; \| & | \;\; \text{H} \\
\text{HC—C} \quad + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4\text{—C—CH} \\
\text{H} \;\; | & | \;\; \text{H} \\
\text{HCH} & \text{HCH} \\
\text{H} & \text{H} \\
\text{Isobutene} & \textit{tert}\text{-Butyl sulfate}
\end{array}
$$

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{HCH} & \text{HCH} \\
\text{H} \;\; | & \text{H} \;\; | \\
\text{HC—C—HSO}_4 + \text{H}_2\text{O} \rightarrow \text{HC—C—OH} + \text{H}_2\text{SO}_4 \\
\text{H} \;\; | & \text{H} \;\; | \\
\text{HCH} & \text{HCH} \\
\text{H} & \text{H} \\
\textit{tert}\text{-Butyl sulfate} & \textit{tert}\text{-Butanol}
\end{array}
$$
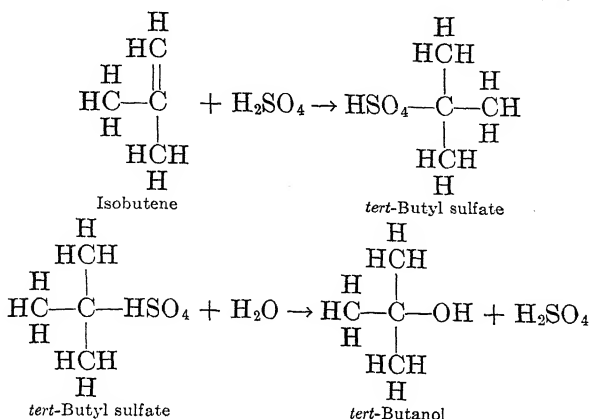
The properties of the alcohols used in aviation fuel are listed in Table 5-VIII.

TABLE 5-VIII.—PROPERTIES OF ALCOHOLS

	Methanol	Ethanol	Isopropanol	tert-Butanol
Boiling point, °F........	148	173	180	181
Calorific value, net, B.t.u.-/lb...................				
Calorific value, gross, B.t.u./lb..............	9,500	12,700	14,400	15,260
Density at 60°F..........	0.797	0.792	0.791	0.789 at 68°F.
Freezing point, °F........	−144	−179	−129	77
Heat of vaporization, B.t.u./lb...............	473	368	287	235
Octane number (A.S.T.M. Motor)...............	98	99	about 100	90–95
Vapor pressure, Reid, lb..	5.3	2.8		
Water solubility.........	Miscible	Miscible	Miscible	Miscible

The calorific values for the alcohols are much lower than those of the corresponding hydrocarbons (22 to 54 per cent lower than isooctane on a weight basis) and are completely miscible with water. This characteristic is a definite disadvantage since water is usually present in fuel storage systems and, if present in sufficient quantities, causes a separation of the alcohol from the blend.

Properties of Aviation Gasoline—Alcohol Blends.—Properties of ethyl alcohol—motor gasoline blends have been investigated thoroughly and the results reported in the literature (see Bibliography in Ref. 7). The investigations of the characteristics of aviation gasoline—alcohol compositions have not been so extensive as those concerned with the motor gasolines. It has been found, however, that in certain respects the alcohol blends have decided advantages as aviation fuels, while in other respects their usefulness is limited.

The octane numbers of the three alcohols reported[6] are very high. The blending octane numbers of methanol and ethanol are higher than that of isooctane, while that of *tert*-butanol is approximately equal to that of isooctane. The lead susceptibilities of the different alcohols in gasoline mixtures vary with the individual alcohols. Ethanol blends have the lowest susceptibility, methanol blends somewhat higher, and *tert*-butanol blends have lead susceptibilities comparable to isooctane blends

TABLE 6-VIII.—LEAD SUSCEPTIBILITIES OF ALCOHOL—GASOLINE BLENDS[6]

	Octane number (A.S.T.M. Motor)			
	Ethyl	Methyl	*tert-*Butyl	Iso-octane
Unblended................................	99	98	..	100
50% blended with 70:				
Octane number straight-run gasoline....	88	89*	83	84
+1 cc. T.E.L./gal....................	89	91*	91	90
+2 cc. T.E.L./gal....................	89	93*	95	94
+3 cc. T.E.L./gal....................	89	95*	97	97
+4 cc. T.E.L./gal....................	89	96*	99	99

* Blend contains 50 per cent 70 octane number straight-run gasoline; 40 per cent methyl alcohol; and 10 per cent ethyl alcohol.

It is interesting to note the almost total lack of response of ethanol blends to tetraethyl lead addition, while the *tert*-butanol alcohol blend, on the other hand, has almost the same response as the isooctane blend.

The thermal qualities of alcohol-gasoline blends depend to a great extent upon the alcohol used. All alcohols (and other

oxygen-containing blending components) lower the heat of combustion of the blend.   For a given weight percentage, methyl alcohol lowers the heat of combustion to a much greater extent than does ethyl alcohol.   The latent heats of vaporization of the blends are increased more by the addition of the lower alcohols than by the higher molecular weight types.

Gasoline blends containing alcohols are unstable in the presence of water because of the tendency of the water to dissolve the alcohol.   In the presence of small amounts of water, the gasoline blend has a greater tolerance for water than gasoline alone and this is a decided disadvantage.

Performance of Aviation Gasoline—Alcohol Blends.—The performance tests of alcohol-gasoline blends indicate that[4]

1. There is a marked freedom from carburetor icing.

2. They do not drop off in power at abnormally rich mixture strengths as rapidly as do the hydrocarbons.

3. They tend to reduce cylinder temperatures because of the high latent heats of the alcohols without serious power loss when operating engines with rich fuel mixtures.

4. They tend to preignite in engines having high cylinder wall temperatures.

5. The power loss (compared to isooctane blends) is great under cruising conditions (with lean mixtures), the degree of loss depending on the quantity and type of alcohol in the blend.

6. The specific fuel consumption is much greater in alcohol blends than with regular types of gasoline (about 4 per cent increase for each 10 per cent of ethyl alcohol contained[7]).   This factor makes it disadvantageous as a cruising fuel.

"SAFETY" OR HIGH-FLASH AVIATION FUELS

It has been long recognized that the high-volatile aviation fuels have presented a distinct hazard in flight, during refueling, or after a crash because of their inflammability.   Many of the fatalities occurring as the result of airplane accidents are caused by the flashing and burning of the fuel after a crash.   The danger of fire is always present in pouring or pumping the fuel into the aircraft fuel tanks.   At various times investigations have been conducted to determine the manner in which such fires start, and probably the most classical of these investigations were those conducted by the Army Air Forces at Wright Field.

In these experiments full-sized airplanes were warmed up, run down an incline, and crashed into a concrete wall, the crash being photographed with high-speed cameras. Although these experiments were valuable relative to the particular type of airplane and fuel used, the conclusions obtained were not adaptable to all types of airplanes and fuels.

Although the case of fires after a crash may be due to the ignition of lubricating oil coming in contact with exhaust or other hot engine parts,[12] or the flashing of the fuel upon similar contact, the actual damage results from the explosive burning of the gasoline. The volatile gasoline of the type in general use today tends to burn explosively because of its low flash point and high volatility, and this has caused a great amount of interest in the so-called "safety" or "high-flash" aviation fuels.

There has been much discussion concerning the adaptability and use of safety fuels for aircraft from the standpoint of safety and performance in aircraft engines, but insufficient data have been presented to enable any definite conclusions to be drawn. It has been stated[12] that the use of high-flash fuels would eliminate the danger of explosions due to the collection of vapors in the wings and other portions of the airplane and their ignition from a spark or a static charge. On the other hand, the danger of the formation of explosive mixtures in the fuel tanks would be greater with the lower volatility fuel than with the high-volatility fuel, since the vapor mixture formed above the high-volatility fuel would be too rich to support explosive combustion.

Characteristics of High-flash Aviation Fuel.—From the safety viewpoint very little definite information is available on the necessary characteristics of high-flash aviation fuel, but it is generally accepted that flash point and spontaneous ignition temperature are two factors intimately connected with the fire hazard and are the principal characteristics to be considered. In the case of an aircraft fire occurring after a crash, in flight, or during refueling due to a spark or flame, the flash point is the controlling factor since it indicates to a great extent the ease of formation of combustible mixtures. Where the fire starts as the result of fuel contact with hot engine parts and in the absence of a flame, the spontaneous ignition temperature of the fuel is the more important characteristic. Table 7-VIII lists several fuel types with their spontaneous ignition temperatures.

TABLE 7-VIII.—SPONTANEOUS IGNITION TEMPERATURES OF VARIOUS FUELS[12] AND FUEL MATERIALS

	Octane No., A.S.T.M. Motor	Flash point, °F.	I.B.P. °F.	Spontaneous ignition temp., °F.
Paraffinic high-flash fuel, unleaded........................	99	110	330	930–1030
+3 cc. T.E.L./gal...........	100 + 2 cc.*	110	330	990–1030
Aromatic high-flash fuel unleaded.	75	110	338	790–1030
+3 cc. T.E.L./gal...........	86	110	338	880–1030
C.P. isooctane unleaded.........	100	...	211	970–1030
+3 cc. T.E.L./gal...........	100 + 3 cc.*	...	211	1060–1100
Isooctane, straight-run blend, unleaded........................	85	...	...	910–1030
+3 cc. T.E.L./gal...........	100	...	...	960–1030

* Isooctane + − cc. T.E.L./gal.

It is interesting to note that the spontaneous ignition temperatures of the high-flash fuel types are not greatly different from those of the high-volatility-fuel types of equal octane number. Therefore, from that standpoint at least, the safety fuel has no decided advantage over the high-volatility type.

The principal qualities of the high-flash fuel which influence aircraft engine performance are (1) octane number, (2) volatility, and (3) heating or combustion value. According to present trends the safety fuel must have an octane number at least equivalent to that of the higher grade of high-volatility aviation gasolines. This means that it should have an octane number around 90 to 100. The volatility must be low to ensure a relatively high flash point. This requires a different method of introducing the fuel into the engine cylinders than that used for the regular high-volatility type of fuel, if the losses in power and depreciation of octane number due to air or mixture preheating are to be eliminated. The injection systems for high-flash fuels are reported[13] to give good fuel distribution, good acceleration characteristics, and freedom from icing. Starting difficulties are encountered with low-volatility fuels, and, as a result, starting is usually effected by the use of light gasoline.

Proper combustion characteristics are as important in high-flash aviation fuel as in the regular aviation gasoline. A high

heat of combustion is necessary to ensure a reasonably low specific fuel consumption.

Other general qualifications for safety fuel are the same as those for the regular aviation gasolines and consist mainly of stability toward oxidation and gum formation, low sulfur content, low freezing point, noncorrosiveness, and good lead susceptibility.

Table 8-VIII lists the characteristics of an average type of safety fuel.

TABLE 8-VIII.—CHARACTERISTICS OF HIGH-FLASH AVIATION FUELS

Calorific value, net, B.t.u./lb	18,300–18,700
Corrosion	None
Distillation, A.S.T.M.:	
I.B.P., °F., min	300–320
E.P., °F., max	400–420
Flash point, °F., min	105–110
Freezing point, °F., min	−76
Gum, accelerated, mg./100 ml., max	5.0–6.0
Gum, copper dish, mg./100 ml., max	5.0–6.0
Octane number*	90–100
Sulfur, %, max	0.05
Tetraethyl lead, cc./gal., max	3.0–4.0

* A.S.T.M.-C.F.R. Aviation method.

The qualities listed in Table 8-VIII correspond to those of the higher grades of high-flash aviation fuel produced in the past five years, and, with the exception of boiling range and flash point, they are the same as required for the regular aviation gasoline. No definite specifications for an ideal safety-type aviation fuel have been agreed upon because of the lack of data on engine operation with this type of fuel. Heron and Beatty[14] give the opinion that the flash point cannot be lowered below 110°F. without reducing the safety factor, nor can the end point be increased as it would cause unsatisfactory engine performance. Ellis and Sweeney[15] suggest the use of higher end-point fuels to increase the available supply.

Manufacture of High-flash Aviation Fuels.—Aviation safety fuels made from aromatic crude oils and by synthetic methods were used to a limited extent in Europe for several years before a fuel of this type was introduced into this country. In 1929 the Standard Oil Development Co. marketed an aromatic high-flash aviation gasoline which was made by high-temperature hydrogenation and which had an octane number of approximately 90.

Until the late thirties the interest of both the aviation industry and the petroleum industry in safety fuel was mostly academic, and there was very little of this type of fuel (compared to the conventional type) manufactured and used. This apparent lack of interest was due to several factors. Although it was recognized that a fire hazard existed with the use of the high-volatility fuels, no definite steps had been taken to determine what constituted a "safe" fuel. The aviation industry was also reluctant to adopt the use of a gasoline of which there was only a relatively small supply in the quality desired and whose cost was high. The petroleum industry on the other hand was not greatly interested because of the high manufacturing cost of such a fuel and the small demand.

With the advent of hydrocarbon conversion processes in petroleum refining it was found that large quantities of suitable safety fuel could be produced as a by-product from the manufacture of high-octane aviation base stocks and from isooctane manufacture at a lower cost, and this attracted the interest of the aviation-fuel users and producers. Because of this renewed interest within the past few years, there have been many investigations conducted by the refining industry to determine possible ways of manufacturing this type of fuel.

There are at present two principal classes of high-flash aviation fuel being produced: (1) aromatic and (2) paraffinic.

AROMATIC TYPE.—Aromatic-type safety fuels are those fuels which contain 20 per cent or more of aromatic hydrocarbon compounds. They may be produced from selected aromatic crude oils by extraction-distillation methods, or by conversion methods from any type of crude oil. It has been estimated[12] that over 400,000,000 gal. per year of 300 to 400°F. boiling-range aromatic safety fuel is potentially available from aromatic crude oils along and around 200,000,000 gal. yearly potentially available from cracking and reforming processes.

Some of the methods capable of producing aromatic safety fuels are listed as follows:

1. Extraction processes:
    a. Sulfur dioxide
    b. Furfural
2. Conversion processes:
    a. Catalytic aromatization—hydroforming
    b. Thermal aromatization

c. Destructive or high-temperature hydrogenation

d. Catalytic cracking or reforming

e. Thermal reforming—polyforming—gas reversion.

Extraction.—Extraction processes utilizing solvents having a high degree of selectivity for aromatic hydrocarbons may be used to produce aromatic safety fuels. In this method selected aromatic crude oils are fractionated to secure a cut of the correct boiling range, and this cut is extracted with suitable selective solvents such as sulfur dioxide[16] and furfural, which separate the aromatic portion. The aromatic safety fuel base is then recovered from the extract, usually by distillation.

Conversion Processes.—Catalytic aromatization, thermal aromatization, catalytic cracking, and thermal reforming processes are discussed in detail in Chap. V in connection with the manufacture of high-octane aviation-fuel base stocks. The fractions boiling from 300 to 400°F. from the conversion product resulting from most of these processes make a satisfactory safety fuel. To procure higher yields of this fraction the conditions of operation of the processes must be changed somewhat.

High-temperature hydrogenation,[17] a process producing a high-octane heavy naphtha through catalytic destructive hydrogenation at high temperatures, was the first source of aviation safety fuel in this country. In this process the charging stock, usually consisting of recycle gas oils, heavy cracked naphthas, or similar materials, is subjected to temperatures of 932 to 1040°F. in the presence of a catalyst (not specified, but probably oxides or sulfides of such metals as molybdenum, tungsten, cobalt, and nickel and hydrogen) under pressures of 3,000 to 5,000 lb. per sq. in. The resulting products (depending upon the characteristics of the charge stock and catalyst) are a highly aromatic gasoline fraction and gas composed of lighter hydrocarbons and hydrogen. The yield of gasoline ranges from 58 to 71 per cent. One gasoline[17] produced by this method, 80 per cent of which distilled above 212°F., had an octane number of 80 but had a very low lead susceptibility. The low lead response was due to the presence of aromatic compounds.

The yields of aromatic safety fuel available from conversion processes depend upon many factors: the type of process, the charge material, the operating conditions, and whether or not the process is operated to produce safety fuel or some other

product with the safety fuel produced as a by-product. The quality of the fuel depends largely upon its method of manufacture. Table 9-VIII lists the characteristics of aromatic safety fuels made by several different methods.

TABLE 9-VIII.—PROPERTIES OF AROMATIC-TYPE HIGH-FLASH AVIATION FUELS

	SO$_2$ Extraction S. Texas naphtha[16]	Houdry catalytic cracking[18]	High-temperature hydrogenation[17]	Polyforming[19]
Composition:				
Aromatics..............	} 84.0	36	(50–75)	(20–25)
Olefins................		4		
Paraffins and naphthenes.	16.0	60		
Tests:				
Acid heat, °F...........	......	.....	.....	2
Corrosion..............	None	None	None	None
Distillation (A.S.T.M.):				
I.B.P., °F............	247	330	309	301
10%, °F.............	267	341	.....	311
50%, °F.............	292	353	.....	326
90%, °F.............	337	376	.....	372
E.P., °F.............	394	397	411	426
Flash point, °F........	......	105	107	
Gravity, A.P.I..........	33.7	35.9	28.5	36.2
Gum, copper dish, mg./ 100 ml...............	......	.....	4.8	
Heat content (gross), B.t.u./lb. (calc.)......	......	19,620		
Octane number (A.S.-T.M.):				
Unleaded............	91.1*	76.5	93	80
+1 cc. T.E.L./gal.....	......	81.5	.....	86
+2 cc. T.E.L./gal.....	......	83.5	.....	87
+3 cc. T.E.L./gal.....	......	84.5	.....	88
+6 cc. T.E.L./gal.....	......	86.5	.....	

* C.F.R. method.

The stocks having octane numbers from 85 to 90 may be leaded to a 90 to 95 octane number with the addition of 4 cc. of T.E.L. per gal. In general, the aromatic high-flash fuels have poor lead susceptibilities and have heat values 7 to 9 per cent lower than the paraffinic types. It is claimed that the Houdry

catalytic fuel listed in Table 9-VIII has only 1.5 to 2.0 per cent lower heating value than a similar boiling-range paraffinic safety fuel.

PARAFFINIC TYPE.—Suitable high-flash paraffinic-type aviation fuels cannot be obtained directly from crude oil distillation or extraction since the octane number of the paraffin compounds contained in the heavy naphthas is much too low. (Properties of a high-boiling-range straight-run naphtha are given in Table 10-VIII.) Therefore, the high-octane paraffinic types of high-flash fuel must be produced by conversion methods. Suitable high-octane safety fuels have been produced by catalytic alkylation and catalytic polymerization plus hydrogenation. Another possible process source is that of haphtha isomerization.

Under present conditions of operation whereby the various isooctanes are the principal product, there is available over 50,000,000 gal. yearly of 80 to 90 octane number alkylate and hydrogenated polymer having a boiling range of 300 to 400°F. This estimate was given by Hubner[12] in 1940 and was based on the yields from the isooctane production at that time. Production has increased greatly in the last two years, and it is probable that the potential by-product production of paraffinic safety fuels at present or in the near future will be around 250,000,000 to 300,000,000 gal. yearly.

Conversion Methods for Manufacture of Paraffinic Safety Fuel.— The two principal methods suitable for the manufacture of paraffinic safety fuel are catalytic alkylation, and selective polymerization and hydrogenation. A third possible process is naphtha isomerization. These processes are all described in detail in Chaps. V and VI in connection with the manufacture of the conventional high-volatility aviation fuels.

In the alkylation process the formation of isooctanes is accompanied by the formation of isododecanes, and the yield of heavy alkylate usually amounts to 10 to 15 per cent of the total alkylate produced. This isododecane fraction boils between 300 and 400°F. and has an octane number ranging from 80 to 95, depending upon the molecular configuration.

Catalytic polymerization also produces 12-carbon-atom olefin polymers which when hydrogenated have suitable boiling ranges and octane numbers of 85 to 95. The yield of this material based upon the total polymer is around 10 to 15 per cent.

No data have been published on the catalytic isomerization processes for naphtha in regard to their application to safety fuel manufacture, but it is probable that a considerable yield of high-flash paraffinic aviation fuel could be produced which would have a high unleaded octane number and good lead susceptibility.

It should be remembered that the yields given above are those for the by-product manufacture of the safety-fuel fraction. It is entirely possible, should the economic picture change in regard to general acceptance of this type of fuel, that the processes could be changed to the manufacture of the higher boiling high-flash aviation fuel, and the present yields of this material and the yields of isooctane fraction probably could be reversed.

Another possibility for the manufacture of larger quantities of high-octane safety fuels is that of blending high-octane hydrocarbons having the required volatility characteristics with stocks of lower octane number having good lead susceptibilities, and raising the octane number of the blend to the necessary value by the addition of tetraethyl lead. This procedure is comparable to that followed in the manufacture of high-octane high-volatility aviation gasolines and offers a method of reducing costs and increasing volume.

Table 10-VIII shows the lead susceptibility of a hydrogenated triisobutene-straight-run blend.

TABLE 10-VIII.—LEAD SUSCEPTIBILITY OF 50:50 BLEND OF STRAIGHT-RUN NAPHTHA AND HYDROGENATED TRIISOBUTENE

	Octane Number (A.S.T.M. Motor)
Unleaded	84.0
+1 cc. T.E.L./gal	90.5
+3 cc. T.E.L./gal	96.0

Table 11-VIII lists the characteristics of some typical paraffinic high-flash aviation fuels produced by different processes.

In general, the paraffinic high-flash safety fuels have octane numbers from 80 to 100 and the lead susceptibilities are high enough to enable the lower octane stocks to be raised to 95 to 100 octane number by the addition of 4 cc. of tetraethyl lead per gallon. These fuels are stable, are low in sulfur content, and have high heats of combustion.

Performance of High-flash Aviation Fuels.—High-flash fuels are difficult to vaporize and therefore are not satisfactory for use

in regular carbureted motors.   With the use of injection systems it is believed that such fuels will perform equally as well or better than the high-volatility fuels of equivalent octane number.   Starting difficulties will be a factor in the use of high-flash fuels, but these may be overcome by the use of an accessory starting fuel.

TABLE 11-VIII.—PROPERTIES OF PARAFFINIC-TYPE HIGH-FLASH AVIATION FUELS

| | Straight run[12] | U.O.P. polymerization hydrogenation[12] | | Isodo-decane[12] | Hydro-genated triiso-butene[12] | Alkyl-ate[20] |
		1*	2†			
Acid heat, °F............	.....	.....	.....	.....	.....	2
Distillation (A.S.T.M.):						
I.B.P., °F...........	332	273	250	342	349	310
10 %, °F............	340	317	281	.....	.....	327
50 %, °F............	350	389	361	.....	.....	343
90 %, °F............	375	389	361	.....	.....	362
E.P., °F............	400	450	390	342	350	384
Flash point, °F........	.....	.....	.....	.....	.....	103
Gravity, A.P.I........	37.9	50.5	58.1	55.7	58.3	57.0
Gum, accelerated, mg./100 cc..........	.....	.....	.....	.....	.....	2
Octane number (A.S.T.M. Motor):						
Unleaded...........	68.5	89	96	100	100	81
+1 cc. T.E.L./gal....	74.5	.....	.....	.....	.....	86
+2 cc. T.E.L./gal....	79.0	.....	.....	.....	.....	89
+3 cc. T.E.L./gal....	81.0	.....	.....	.....	.....	92
+4 cc. T.E.L./gal....	82.5	.....	.....	.....	.....	94

* 1 part isobutene to 2 parts n-butene.
† 4 parts isobutene to 1 part n-butene.

One hundred octane high-flash fuels are said to give the same power output as is given by isooctane when injection is used for both fuels.

Future of High-flash Aviation Fuels.—Although high-flash or safety aviation fuel has been available in this country since 1929, it has not achieved a position of prime importance in the aviation-fuel picture.   Its widespread use has been objected to on such grounds as high cost, insufficient quantities available, starting difficulties, questionable performance in existing-type

motors, and the questionable degree of safety attained by its use.   As a result no definite requirements have been established for such fuels.   It is possible that, if an agreement is reached, primarily among users of aviation fuels, as to what constitutes a "safety" fuel, and these specifications are given to the petroleum industry, that industry will be able to supply all the fuel necessary for their requirements at a cost comparable to the equivalent grade of high-volatility aviation gasoline.

It is also probable that certain changes in engine design will be required, particularly in regard to the method of introduction of fuel into the engine, but this should offer no great difficulties.

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CHAPTER IX

PERFORMANCE OF AVIATION GASOLINE

The petroleum industry is naturally more interested in the methods of production and the quality of the aviation gasolines that it produces than in the performance of the different types of fuels in aircraft engines. However, the quality of the fuel from the standpoint of the producer and the performance value from the standpoint of the user are very closely related, and it is well for the producer to be familiar, at least in a general way, with the performance in aircraft engines. Similarly, it is well for the user to know something about the manufacture of the fuel upon which he is dependent for efficient operation of his engines. Under this condition a common ground for further research and developed is attained.

Much of the advancement of aviation has been attributed to the ability of the refining industry to supply fuels of higher quality and at relatively lower cost as the need for them arose.

TABLE 1-IX.—DEVELOPMENT OF THE WRIGHT CYCLONE ENGINE, 1929–1939*

Year	Horse-power	Speed, r.p.m.	B.M.E.P., lb./sq. in.	Sp. wt., lb./hp.	Sp. fuel consumption, lb./hp./hr.	Octane number of fuel
1929	535	1,900	112	1.5	0.50	73
1930	580	1,900	120	1.4	0.50	80
1931	600	1,960	130	1.3	0.50	80
1932	650	1,950	140	1.25	0.50	87
1933	700	1,950	150	1.20	0.48	87
1934	780	2,100	150	1.30	0.46	87
1935	820	2,100	160	1.20	0.46	87
1936	1,000	2,200	185	1.15	0.44	87
1937	1,100	2,300	200	1.10	0.43	90
1938	1,150	2,400	210	1.05	0.41	90
1939	1,200	2,500	210	1.00	0.40	90

* Taken from curves appearing in "Lubrication," The Texas Co., September, 1940.

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This has enabled the aviation engineers to improve the design of their motors, resulting in more power, greater efficiency and economy, and lighter weight.

The data given in Table 1-IX illustrate the development of the Wright Cyclone engine over a 10-year period.

Other engine makes and types show a comparable development over the same period of time in regard to horsepower output, speed, specific weight, and specific fuel consumption. At the present time airplanes are being equipped with 2,000-hp. engines with a low specific weight (weight per horsepower) and a low specific fuel consumption. Such improvements in engine design are due to a great extent to the constant improvement in anti-knock quality of aviation gasolines and the guaranteed availability of such fuels by large production capacity.

RATING FUEL PERFORMANCE

The various tests and specifications for aviation gasoline discussed in Chap. III are those which are used as controls in the manufacture and sale of the fuel. Such tests for quality are not directly indicative of the fuel's performance in actual engine and flight tests, but they are used in place of performance tests because of the difficulties involved in the conducting of full-scale engine tests by the producer. The specifications for aviation gasolines based on laboratory tests have been established as closely as possible in compliance with the desirable qualities of the fuel on the basis of performance tests in full-scale engines and under flight conditions. Thus, for example, it has been found that in a particular design of engine, it is necessary to have a fuel of 100 octane number to obtain the operating characteristics for which it was designed; a fuel having an octane rating 100, therefore, is specified. Similarly, the cruising range of an airplane is limited by the number of heat units that can be contained in its fuel tanks; therefore, a fuel having a high heat of combustion (in B.t.u. per pound) is specified.

These specifications are definite insofar as the laboratory is concerned, but they still do not indicate the actual performance in terms of engine and airplane operation, and it is from this standpoint that the actual value of the aviation fuels is determined.

Fuel Characteristics Affecting Performance.—The principal performance characteristics of aviation gasolines are

1. Maximum power output.

2. Economy or consumption per unit of power produced.

3. The physical and chemical characteristics that to some extent affect engine operation, such as freezing tendency, vapor locking, gumming tendency, and corrosion.

POWER.—The fuel characteristic that is the most important in regard to power output in an aviation engine is its antiknock value. Fuels of higher antiknock value allow greater compression ratios to be used with resulting increase in power and efficiency, and overheating and knocking effects are eliminated, which results in an added increase in power.

Antiknock Value—Motor Knocking.—The phenomenon of "knocking" in engines is definitely connected with the characteristics of the fuel. Knocking, sometimes called *detonation*, is the term usually applied to the audible "pinging" occurring when the fuel is exploding in the cylinder at a rate in excess of that necessary for correct operation. Preignition may also cause knocking and may be classed as this type of phenomenon. However, there is a considerable difference from the standpoint of the fuel, since knocking and detonation take place after ignition from the spark plug, while preignition takes place before the fuel is ignited by the ignition system.[1] This may be caused by hot carbon or hot spark-plug wires. In addition to knocking and preignition, Stansfield and Thole[2] include autoignition, which is the result of spontaneous ignition of the fuel in the absence of a spark or flame.

There are two principal theories on the mechanism of knock: (1) the spontaneous-ignition theory and (2) the chain-reaction theory. In the first the fuel is said[3] to knock as the result of an explosion caused by partial burning of the fuel, the compression and heating of the unburned fuel by the burning gases, and the spontaneous explosive burning of the unburned portion when the critical conditions of temperature and pressure are reached. In the second the knock is said[4] to be due to the formation of oxidized products (peroxides, aldehydes) to critical concentrations which accelerate the burning rate of the unburned fuel enormously, causing a high-velocity explosion resulting in knocking.

Regardless of the mechanism, it is evident that the knocking tendency of fuels is directly dependent upon the characteristics

of the hydrocarbons that it contains.   (The antiknock properties of the hydrocarbons were discussed in Chap. IV.)

From the standpoint of the fuel its ability to resist knocking is its most important characteristic in regard to its potential power output.   Fuels having antiknocking characteristics allow the use of higher compression engines, and therefore give much greater power due to the increase in the efficiency of the Otto cycle when greater compression ratios are utilized.   The cal-
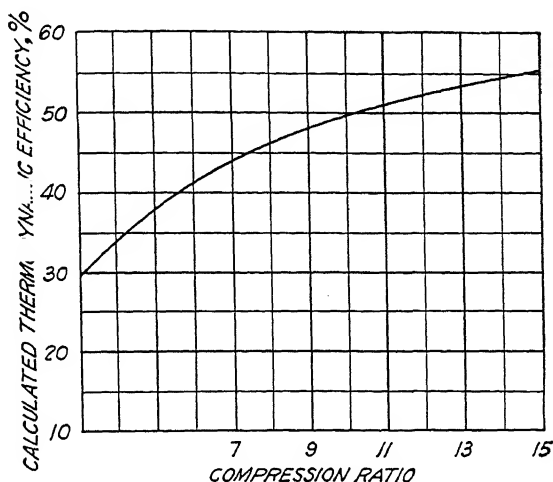
FIG. 1-IX.—Thermodynamic efficiency for the Otto cycle at different compression ratios.   (*Courtesy of Petroleum Engineer.*)

culated thermodynamic efficiencies[4a] based on compression ratio for the Otto cycle are shown in Fig. 1-IX.

Thus it is evident that fuels of higher antiknock rating will give greater power output in engines designed for their use (*i.e.*, with higher compression ratio) than those of lower antiknock value in engines designed for their use (*i.e.*, lower compression ratios).

Octane Number.—In Chap. III the methods of rating fuels according to their antiknock values were discussed.   In general, all antiknock values are given in terms of octane number.   This represents the percentage of isooctane in an issoctane *n*-heptane blend which has the same antiknock characteristics as the test fuel when both are compared in an engine under closely controlled conditions.   In other words, the octane number of a fuel

is a rating on an arbitrary scale which does not necessarily have a direct relationship to its antiknock value in actual engine operation. The variety of methods that have been developed indicate that a constant attempt has been made to more closely approximate actual full-scale engine octane numbers.
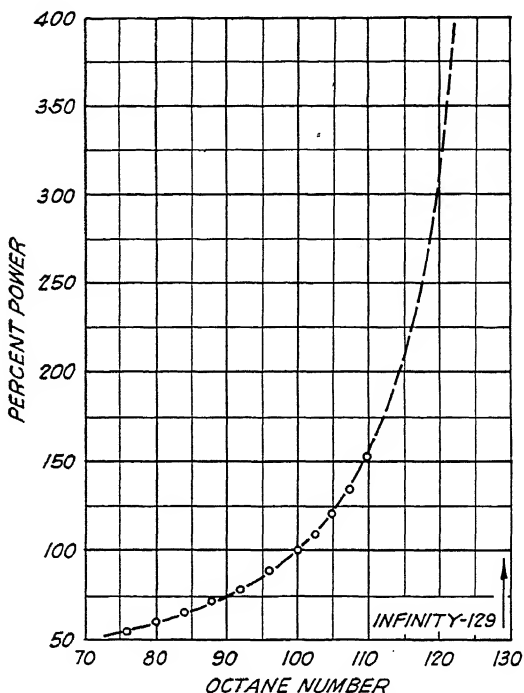
Fig. 2-IX.—Relationship between octane number and power output. (*Courtesy of J. Aeronaut. Sciences.*)

Octane numbers and potential maximum power output of the fuels do not bear a straight-line relationship. This is shown by Fig. 2-IX.*

* This curve was determined[5] by plotting the inverse of the I.M.E.P. $\left(\dfrac{1,000}{\text{I.M.E.P.}}\right)$ against the octane number of technical isooctane with equal increments of tetraethyl lead added and determining the octane numbers above 100 on the arithmetic scale. The intercept of the resulting straight line with the octane scale axis for engine conditions of 1,800 r.p.m., 385°F. jacket temperature, supercharged, occurs at approximately 129 octane number.

We see from this curve that the power output increase between two fuels, one of 90 octane number and one of 100 octane number, is approximately 2.5 times the increase between two fuels of 70 and 80 octane number.   The increased power between two fuels of 100 and 110 octane number is 5 times that between 70 and 80 octane number.   Based on an arbitrary designation of 100 per cent power output for the 100 octane number fuel, the 70 octane number fuel will give only 50 per cent power and the 100 octane fuel 150 per cent.

This difference is particularly significant in fuels having octane numbers around and above 100 where the relative size of the octane number in terms of power increases greatly with each unit until an infinite power increase per unit is shown around an octane number of 129.

It is obvious that octane number by definition is ineffective as a rating standard above 100 since this represents pure iso-octane.   Several methods of extrapolation of the octane scale have been devised, such as those of Trimble and Richardson,[6] Heron and Beatty,[5] and Cattaneo and Stanley,[7] which use the known power increase achieved by additions of tetraethyl lead above that shown by fuels of 100 octane number.

Therefore, it is evident that octane number means nothing in itself in regard to actual performance in an engine and it must be expressed in terms of some function of engine operation (whose operating conditions are defined), such as horsepower (B.H.P., I.H.P.) and compression pressure (I.M.E.P., B.M.E.P.).   This is particularly true in the fuel antiknock range around and above 100 octane number, and this is the range in which interest is greatest in connection with high-quality aviation gasolines.

It is well to bear in mind also that antiknock value in terms of power is dependent upon the design of the engine in which the fuel is to be used.   In a low-compression engine designed to operate on a fuel of 70 octane number the power produced would be little if any greater when a fuel of 100 octane number is used. In an engine of higher compression ratio the 100 octane fuel will produce almost twice the power that is produced by the 70 octane in an engine designed for its use.   On the other hand, the 70 octane number fuel will not function in the higher compression-ratio engine because of the knocking and overheating accompanying its use under those conditions.

ECONOMY.—The question of fuel economy or specific fuel consumption of two gasolines of different characteristics in the same motor is of extreme importance in long cruising flights. The heat of combustion of the fuel is the principal controlling factor in considering the specific fuel consumption under comparable conditions. On a strict comparison basis the heats of combustion can be compared only for fuels of equal antiknock rating, and in general the economy of a fuel based upon its heat of combustion may bear a direct relationship to its antiknock value in full-scale engine operation. For example, a fuel having a high heat of combustion with a low-antiknock value will evidence less economy in operation than one of somewhat lower heat of combustion but with a much higher antiknock value.

The hydrocarbon types included in aviation gasolines determine their heats of combustion. In general, in comparing the hydrocarbon compounds on the basis of the same number of carbon atoms according to the decreasing heats of combustion (B.t.u. per pound), the following order is found:

	Per Cent
Paraffins	100
Olefins	98.5
Naphthenes	97.0
Aromatics	85–90
Alcohols, ethers, and ketones	50–85

This is a direct comparison on the basis of heats of combustion per pound of compound. If full-scale engine octane number is taken into consideration, as it must be in considering aviation gasolines, the order of the compounds is somewhat changed and the differences are not so great.

GENERAL PERFORMANCE.—Although power and economy are the two principal performance factors that are directly dependent on fuel characteristics, there are many others which cannot be classed as performance factors but which have a marked influence on engine operation and which are dependent to some degree on fuel characteristics. The more important of these are (1) carburetor icing and fuel-system freezing, (2) fuel distribution to the cylinders, (3) vapor locking, (4) corrosion, and (5) engine deposits.

Carburetor and Fuel-system Freezing.—From the standpoint of the fuel, carburetor icing and fuel-system freezing are influ-

enced by several factors: (1) volatility of the fuel, (2) solubility or miscibility of water in the fuel, (3) ability of the fuel to retain at low temperatures the water dissolved at higher temperatures, and (4) the freezing point of the fuel.   As a general rule, the gasolines of higher volatility tend to cause more carburetor icing difficulties than those of lower volatility.[8]   The gasolines having greater miscibility with water may be said to have greater ice-forming tendencies in the carburetor and fuel system than those of low miscibility.   This is true only of hydrocarbon-type gasolines because the amount of water dissolved in them is indicative of the amount precipitated at the low temperatures encountered in high-altitude flying.[5]   This tendency is practically eliminated in fuel blends containing alcohols and ketones which have a relatively high water solubility but retain the water in solution at low temperatures.   Fuel-system freezing due to the freezing of hydrocarbon constituents is not a problem where the freezing point of the fuel is below $-76°F.$, which is the temperature specified for all aviation fuels.   The use of benzol and *tert*-butanol as blending agents is limited because of their high freezing points.

When injection systems are employed in place of carburetors, carburetor icing is eliminated; thus, it is no problem when the safety or high-flash types of fuel are utilized, since their use involves injection.

Fuel Distribution to the Cylinders.—The fuel distribution in the manifold when carburetors are used depends primarily upon the volatility range of the gasoline for any given engine condition. Higher volatility fuels give better distribution, while those of lower volatility give poorer distribution and cause uneven engine operation, particularly when operating at low temperatures such as are encountered in high-altitude flying.   The distillation specifications control volatility of aviation gasolines within a suitable range; with the use of accessory heating, the problem of suitable distribution is of minor importance.   The use of injection systems in place of carburetors for utilization of either high- or low-volatile fuels ("safety" fuels) ensures good fuel distribution.

Vapor Locking.—Vapor locking is caused by high vapor pressure gasolines operating at temperatures at which their vapor pressures exceed atmospheric.   This causes formation of vapor

in the fuel lines and interrupts the supply of fuel to the engine. The vapor pressure specification of 7.0 lb., Reid, is sufficiently low to prevent vapor locking in most instances, but there is some difficulty encountered at high altitudes and at high rates of climb where the atmospheric pressure is greatly reduced while the temperature of the fuel is approximately that at ground level.

Injection systems do not have a great effect in the reduction of vapor-locking tendencies since vapor locking usually occurs in the fuel-transmission system.[8]

Corrosion.—Corrosive effects of the fuel used in aviation gasolines may be due primarily to sulfur content and tetraethyl lead. The sulfur content of the fuels is specified at a very low permissible value, since even small amounts of some of the sulfur compounds cause corrosion in carburetors and in exhaust systems where they exist as sulfurous acid. The corrosion and total sulfur content specifications have practically eliminated sulfur-corrosion effects in present-day aviation gasolines.

Some corrosion effects, such as valve and piston pitting and spalling, have been attributed to the use of tetraethyl lead although the degree of the corrosion due to this cause has not been definitely reported in the literature. Hubner *et al.*[8] states, "In general it may be said that less than 1 cc./gallon gives little corrosion; 3 cc. gives more than three times as much; and 6 cc. gives more than twice as much as 3 cc./gallon."

Engine Deposits.—Engine deposits attributable to the fuels may be caused by gums in solution, by materials that form gums and resins under motor-operating conditions, by inhibitors that may tend to form deposits, and by tetraethyl lead. Sulfur compounds that form lead sulfide that is not volatilized into the exhaust system are a secondary contributing factor in this respect.

Marley and Gruse[9] reported the following results obtained from the study of the operation of a small single-cylinder engine on regular motor fuels containing various amounts of gum ranging from 3 to 35 mg. per 100 ml.: (1) at low mixture temperatures no deposits were formed on the valves or in the combustion chamber from any of the fuels; (2) the 3-mg. fuel deposited no gum under any condition of operation; (3) the deposits in both valves and combustion chamber increased as the mixture temperature increased; and (4) more gum was deposited on the valves at richer mixtures.

Since higher mixture temperatures are employed in aviation engines, it is to be assumed that for a comparable gum content the engine deposits would be greater particularly on the valves. The allowable gum content must be less in fuels operating in engines using high-mixture temperatures than in those using lower temperatures.

Deposits caused by the use of tetraethyl lead are somewhat reduced by the inclusion of organic halides in the ethyl fluid which form vaporizable lead halides under combustion conditions. These pass out through the exhaust system. Some deposits are formed, however, and, although this condition may not be desirable from the standpoint of engine operation and maintainance, there is not much that can be done about it until an aviation gasoline is developed at a low cost without the use of tetraethyl lead and having antiknock characteristics of the quality desired.

Performance Testing.—Fuel-performance testing involves the evaluation of fuel characteristics in terms of engine performance. Antiknock value, power output, and economy are all determined by means of engine tests under simulated flight-operating conditions. Flight tests are used to determine airplane performance. Both single-cylinder engines and full-scale engines are used to determine fuel quality under operating conditions.

Single-cylinder Engine Tests.—The single-cylinder liquid-cooled engine tests (without the use of supercharging) are used primarily to determine the antiknock rating of motor and aviation gasolines and are used as laboratory control methods. There have been five principal single-cylinder engine tests devised for this purpose: (1) C.F.R. Research method; (2) British Air Ministry method; (3) U.S. Army Air Forces method; (4) A.S.T.M.-C.F.R. Motor method; and (5) the A.S.T.M.-C.F.R. Aviation method. The engines used in these methods and their operating conditions are described in Chap. III. All have been successful to some degree in interpreting the antiknock value of motor and aviation gasolines in terms of actual full-scale engine performance. However, it has been recognized that these methods are all somewhat insensitive to octane numbers around and above 100 and consequently are not capable of evaluating high-octane fuels in terms of full-scale engine octane numbers.

In considering aviation gasolines of 100 octane number and higher it was necessary to develop methods that had the required sensitivity.

As the result, single-cylinder liquid-cooled engine tests using supercharging have been studied by the Cooperative Fuel Research Committee for some time. In 1938, Heron and Beatty[5] reported that the Ethyl Gasoline Corp. was using a supercharged single-cylinder (C.F.R.) engine to study fuels of high-octane number operating under two sets of conditions: (1) 900 r.p.m. and 212°F. jacket temperature and (2) 1,800 r.p.m. and 385 to 400°F. jacket temperature. The tests were conducted by raising the intake pressure (supercharge) until light knocking, preignition, afterfiring, or backfiring occurred. The fuels were rated upon the indicated power at which any one of these took place. Under condition (1) it was found that benzene, toluene, methanol, and diisobutene were equal to or superior to isooctane plus 6.0 cc. T.E.L. per gal. in terms of indicated power output. Under condition (2) their antiknock values varied between 90 and that of isooctane (100) plus 1.0 cc. T.E.L. per gal.

This type of test has been further developed by the C.F.R. committee in cooperation with the fuel and aviation industries until it is now accepted as one of the principal test methods for determining fuel-performance quality in relation to power output under a variety of conditions.

Supercharged single-cylinder engine tests do not give an entirely satisfactory correlation with full-scale engine performance, but they enable the rating of fuels having antiknock values above 100 octane number much more accurately than do the test engines operated without supercharging by the actual power output produced at given conditions. They also enable the determination of fuel characteristics which are not determined in the octane rating tests such as tendencies toward preignition, afterfiring, and backfiring. In addition to power output, this method may be used to determine such factors as specific fuel consumption, cylinder temperature, and cylinder pressure under varying conditions.

The octane methods are valuable in rating the antiknock values of motor fuels and gasolines having octane numbers below 100.

Also, they have been valuable in determining the majority of fundamental data concerning the antiknock properties and blending antiknock properties of the pure hydrocarbons which are of primary interest in the development of high-antiknock-value aviation fuels.

A single-cylinder test on a full-scale engine has been used to some extent for fuel evaluation but it does not give so satisfactory results as do the single-cylinder engine tests. One of the principal disadvantages lies in the relatively more complicated procedures necessary in operating a test of this kind.

Single-cylinder engine tests using fuel-injection systems have been used with success, particularly in the investigation of performance of safety or high-flash aviation fuels.[10]

FULL-SCALE ENGINE TESTS.—Full-scale engine tests on both air-cooled and liquid-cooled motors are used primarily by the engine manufactures and aviation industry to rate fuel performance and to determine its operating characteristics. In practically all cases at present supercharging is utilized. These tests may be used for other purposes than the study of fuel characteristics, and this therefore partly compensates for the increased cost of the full-scale motor setup. Such full-scale equipment is not used to a great extent by aviation-fuel manufacturers because of the expense of the equipment, the cost of the individual tests, and the complicated testing procedure requiring highly trained and skillful personnel.

Many fuel-performance characteristics may be determined by full-scale engine tests, but some are of more importance than others. Veal[11] listed the characteristics to be determined in full-scale engine tests (both air-cooled and liquid-cooled) in the order of their importance as follows:

1. Maximum cylinder-head temperature, since this is limited by safe practice.

2. Average cylinder-head temperatures.

3. Average cylinder-head and cylinder-base temperatures.

4. Change in horsepower available as fuel flow is reduced.

5. Specific fuel consumption or fuel consumption per unit of power output.

Gagg[12] classified the engine tests on the basis of cruising ratings and take-off ratings as follows:

Cruising rating:

1. Minimum weight of fuel used per unit of power-time at required output for cruising.

2. Freedom from overheating beyond safe limits.

3. Minimum volume of fuel required.

Take-off rating:

1. Maximum power output.

2. Freedom from overheating.

The equipment for full-scale engine tests is complicated and expensive. It usually involves a full-scale engine with a dynamometer set up for the determination of power output, and all of the accessory instruments necessary for the determination of speed, cylinder pressure, fuel flow, manifold pressure (supercharge), cylinder and head temperatures, and various other data.

The tests are conducted by varying one control operation and holding another constant and determining the variation of the remaining characteristics as a function of the controlled variable operation. For example, horsepower output, cylinder-head temperature, specific fuel consumption, and detonation characteristics may be determined by the controlled variation of mixture proportion with a constant throttle (or fuel flow).

Full-scale engine testing is very flexible and may be operated to determine the correlation between practically any operation characteristics.

AIRCRAFT FLIGHT TESTS.—The study of fuel characteristics in a single-cylinder test engine enables the determination of certain of its performance qualities in regard to antiknock value, specific fuel consumption, and others, and this type of test offers a relatively accurate method of determining and controlling the quality of the fuel from the standpoint of the producer. The full-scale engine tests go further in that the effects of variations in engine design on fuel performance in regard to power output, efficiency, and various full-scale operating conditions are determined. This type of test is of great value in the study of the engine type and characteristics in conjunction with fuel type and characteristics.

The aircraft flight tests are the ones that complete the picture in that the performance of fuels is studied under actual flight conditions. Obviously the conditions encountered in two flights with the same plane using different fuels may not be exactly the

same. However, the data obtained from such tests are of importance because factors that influence fuel performance are encountered under flight conditions that can not be exactly duplicated under laboratory test conditions.

The factors determined in flight tests having a direct relation to fuel characteristics are

1. Rate of climb.
2. Cruising speed.
3. Maximum speed.
4. Maximum altitude.
5. Fuel consumption under cruising conditions.

FUEL PERFORMANCE—ENGINE TESTS

The two principal criteria of aviation-fuel performance as determined by means of engine tests are (1) the maximum power output obtained under conditions simulating those encountered in take-off and climbing and (2) the specific fuel consumption (indicating economy) under conditions such as those encountered in cruising. Many investigations have been conducted to determine the relative performance on the basis of these criteria of fuels of different antiknock rating and different hydrocarbon types.

Maximum Power Output.—In comparing fuels of different antiknock ratings, Bass[13] found that the power increase in a full-scale engine derived from the use of an 87 octane aviation gasoline was 12 to 17 per cent over that derived from the use of a 73 octane number fuel. Klein[14] reported a 15 to 30 per cent increase in maximum power output in full-scale engines using 100 octane aviation fuel instead of a 92 (approximately 87 A.S.T.M. Motor octane number) octane grade. In tests described by Young[15] comparing the relative performance of a 92 octane (87) fuel with that of a 100 octane fuel under various operating conditions in a full-scale, radial, air-cooled aircraft engine, it was found that the power increase derived from the use of the 100 octane fuel ranged from 9.6 to 13.5 per cent.

Dubois and Cronstedt[16] reported the maximum power output derived from fuels of 87 octane number, 100 octane number, and isooctane plus 3 cc. of T.E.L. per gal. in a single-cylinder test engine to be increased 15 per cent by the use of the 100 octane fuel and 29 per cent by the use of the isooctane plus 3 cc. of T.E.L.

per gal. Later tests by Klein[17] on fuels of the same type of different octane numbers in a single-cylinder liquid-cooled, supercharged engine gave the data from which the relative per cent power increases shown in Table 2-IX were derived.

TABLE 2-IX.—PER CENT POWER INCREASE BASED ON FUEL ANTIKNOCK VALUE

Fuel	Octane number	Approximate power %
Army 92 grade..................	92	100
Commercial isooctane............	99.5	120
Army 100 grade.................	100	124
Regular 100 grade aviation blend..	100	131
Isooctane + 3 cc. of T.E.L./gal....	100 + 2 cc.	155
Isooctane + 6 cc. of T.E.L./gal....	100 + 4 cc.	192

A summary of the observed results in power increase due to increased antiknock value of the fuel is shown in Table 3-IX. It should be evident that such a summary is only a general comparison and that the results derived from entirely different engine types and designs and also different test-operating conditions cannot be strictly compared. This summary does indicate roughtly, however, the relative power increase derived from fuels of increasingly higher antiknock value.

TABLE 3-IX.—APPROXIMATE POWER INCREASE AVAILABLE FROM FUELS OF VARIOUS OCTANE NUMBERS

Octane Number	Approximate % of Power
73	100
87	112–117
95	120–125
100	132–150
100 + 3 cc. T.E.L.	200–220
100 + 6 cc. T.E.L.	300–325

This relative increase in maximum power output is based on increasing antiknock value of aviation gasolines of similar characteristics, *i.e.*, of the same hydrocarbon base.

In comparing aromatic aviation gasoline blends with the isoparaffin type having approximately the same octane ratings, Klein[17] found that the aromatic blends gave a much greater

power output than did the paraffinic blends. The comparative data are shown in Table 4-IX.

TABLE 4-IX.—POWER OUTPUT OF AROMATIC AVIATION GASOLINES

Fuel	Octane number	Approximate power, %
92 octane grade, paraffinic........................	92	100
Benzol + Calif. naphtha + 2.2 cc. T.E.L./gal.......	92	161
Toluene + natural gasoline + isopentane + 3 cc. T.E.L./gal....................................	97	194
Toluene + benzol + isopentane + 3 cc. T.E.L./gal..	99	243
100 octane grade, paraffinic......................	100	124

These values were derived from a single-cylinder liquid-cooled test engine operated under the following conditions: speed, 2,500 r.p.m.; compression ratio, 5.83:1; jacket temperature, 250°F.; spark advance, 30 deg.; and mixture temperature, 50°F. The power characteristics are much higher than usual and may have been due to the less severe operating conditions. Bass[13] and others state that the full-scale engine antiknock values of the aromatics depreciate under severe temperature conditions. The power output of aromatics in air-cooled high-cylinder wall temperature engines is generally less than that of the leaded paraffinic-type fuels.

Maximum Economy.—In determining the fuel economy characteristics (or fuel consumption) in engine tests, the engine is usually operated at 60 or 70 per cent power output with the leanest mixture possible without exceeding the maximum cylinder-head temperature established as a safe operating limit, or giving rise to knocking detonation. Under such conditions Bass[13] found that fuel consumption was reduced 10 per cent using an 87 octane fuel in place of a 73 octane fuel at comparable power output. Young[15] reported a specific fuel consumption of 0.475 lb. per B.H.P.-hr. for an 87 octane number fuel and 0.375 lb. per B.H.P.-hr. for a fuel of 100 octane number under comparable conditions. This represents a drop of approximately 21 per cent. Klein[17] reported the specific fuel consumption using 100 octane fuel to be 19 per cent lower than that using an 87 octane fuel under the same power output conditions. In the same paper,

Klein reported that based on maximum power output the toluene blend (toluene, natural gasoline, and isopentane +3 cc. T.E.L. per gal., octane number 100) had a 6.7 per cent higher consumption than the isooctane blend and that, under maximum economy conditions (cruising, approximately 65 per cent of rated engine power), its fuel consumption was 4.5 per cent higher than the isooctane blend.

The relative economy of utilizing aviation gasolines of higher octane number may be seen from Table 5-IX.

TABLE 5-IX.—RELATIVE CRUISING SPECIFIC FUEL CONSUMPTION BASED ON ANTIKNOCK RATING

Octane Number	Specific Fuel Consumption, % Decrease
73	
87	10
100	30

In terms of fuel saving in long cruising flights, Klein[17] gives the data shown in Table 6-IX. These data were calculated from the following assumed figures: for the 100 octane fuel the specific fuel consumption is 0.38 lb. per hp.-hr.; for the 87 octane fuel, 0.44 lb. per hp.-hr. The land-flight airplane has two 850-hp. motors and the transoceanic airplane four 850-hp. motors. Both cruise at 67 per cent of rated power.

TABLE 6-IX

	Octane number, land flight		Octane number, transoceanic flight	
	87	100	87	100
Fuel, lb./hr.	502	434	898	775
Fuel, gal./hr.	84	72	150	120
Fuel saving, lb./hr.	. . .	68	. . .	123

On a flight from California to Hawaii, a distance of 2,410 miles, an airplane cruising at a rate of 140 m.p.h. could increase its pay load 2,118 lb. on the basis of the saving indicated above.

FUEL PERFORMANCE—FLIGHT TESTS

The final criteria of the effect of aviation-fuel characteristics on aircraft performance in flight lies in the actual use of the fuel in

flight.   Undoubtedly, a great number of actual flight tests have been conducted to determine the performance values of various fuels, although there have been very few of these experiments reported in the literature.   One of the most prominent of such investigations was reported by Leaver.[18]   In this test a Kool-haven, two-seater, reconnaissance bomber was operated on two aviation gasolines, one of 87 octane number and one of 100 octane number, and the various operating characteristics of the airplane were noted under similar conditions of flight.   The data reported are found in Table 7-IX.

TABLE 7-IX.—RELATIVE PERFORMANCE—KOOLHAVEN, TWO-SEATER, RECONNAISSANCE BOMBER.   BRISTOL MERCURY XV

Aircraft	87 octane fuel	100 octane fuel
Max. speed at 2,750 r.p.m., m.p.h........	236	260
Altitude for max. speed, ft..............	15,700	17,300
Cruising at 60% max. power, m.p.h......	192	211
At height of, ft......................	15,700	17,300
Rate of climb:		
At sea level, ft./min.................	1,490	2,180
At 6,500 ft., ft./min.................	1,630	2,360
At 13,000 ft., ft./min...............	1,730	2,540
At 19,500 ft., ft./min...............	1,220	2,050
Time of climb:		
To 6,500 ft., min....................	4.2	2.9
To 13,000 ft., min...................	8.0	5.6
To 19,500 ft., min...................	12.3	8.3
To 26,000 ft., min...................	19.4	12.2
Service ceiling, ft.....................	31,800	35,700
Absolute ceiling, ft...................	32,800	36,700
Max. engine output, hp...............	830	1,050
Max. power height, ft................	14,450	15,580

That there is a definite advantage derived from the use of the higher octane fuel is shown by these data.

EFFECT OF ANTIKNOCK VALUE ON PERFORMANCE

The effect of antiknock value of aviation gasolines may be summarized on the basis of two points: (1) take-off and (2) cruising.

Take-off.—It has been shown that a great increase in power is derived from the use of 100 octane fuel over that of the 87 octane fuel.   This may be evidenced in either a reduced take-off distance with a given load or increased load with the same take-off distance.   For large airplanes using 100 octane fuel instead of 87 and based on a 20 per cent power increase, a 45 per cent reduction in take-off distance is attained.[19]

Cruising.—The effect of higher octane gasolines on cruising fuel economy is important in that a 15 to 20 per cent lower fuel consumption is achieved with, for example, 100 octane fuel instead of an 87 octane fuel.   This enables a much greater flight radius for the same weight of fuel load or increases the nonfuel load or pay load possible to transport for the same distance.

ECONOMIC VALUE OF OCTANE NUMBER

The most important consideration concerning fuel performance from the standpoint of the commercial aircraft operator is that evidenced by the increased earning power achieved by the use of higher octane number fuels.   The difference in earning power or economic value is dependent upon numerous factors which are by no means constant, such as,

1. The price differential between the two grades of fuels compared.

2. The length of flight.

3. The proportion of the total pay-load capacity of the airplane.

4. The revenue obtainable per pound of pay load.

5. The increase in power obtained by the use of the higher antiknock fuel.

6. The amount of reduction of specific fuel consumption obtained from the use of the higher antiknock fuel.

Several authorities have calculated the increase in gross earning power per each octane number improvement in the fuel based upon the increase in power and reduction of specific fuel consumption obtained from the use of 100 instead of 87 octane fuel.   The calculated data in all cases tend to indicate an equal increase in earning power per octane number over the range from 87 to 100 octane, thus assigning equal earning power to the increase from 87 to 90 octane number and to the increase from 97 to 100.   This is not absolutely true from the standpoint of

fuel performance because the power increase at the higher octane level is greater than that at the lower and to a lesser degree the specific fuel consumption is less. Therefore, earning power probably should be considered either on the basis of the octane numbers of two specific fuels to be compared or on the basis of the octane-number increase relative to the position on the octane scale. This, in effect, means that, from a performance standpoint, the increased earning power per octane number would be greater between 95 to 100 than it would be between 85 to 90.

The increased earning power of higher octane fuels on the basis of octane number calculated by several authorities is summarized on the basis of a revenue of 5 cents per passenger mile (or 0.025 cents per pound-mile) by Hubner and Egloff[20] in Table 8-IX.

TABLE 8-IX.—INCREASED EARNING POWER OF 100 OCTANE OVER 87 OCTANE FUELS

Authority	Increase in Gross Earning Power per Octane Number Improvement in Fuel, Cents
Bass[21]	4.40
Barnard[22]	2.20
Keith, Carey, and Ward[23]	0.25

Doolittle[24] compared the increase in earning power of an airplane over its life of operation at continuous full-load capacity and found that it would amount to around $800,000 for the conditions assumed. Hubner and Egloff,[20] using Barnard's[22] figure of 2.2 cents per gallon increase in earning power, calculated the increase in earning power under comparable conditions to be $153,000.

These figures, based on assumed conditions of performance and operation, indicate that there is a considerable economic advantage obtained from the use of 100 octane fuel.

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APPENDIX

TEST METHODS FOR EVALUATION OF AVIATION FUELS

The methods given here are brief descriptions of the methods used by both the refining and the aviation industries in evaluating aviation gasolines. Many of the tests are required by the specifications while others are used as accessory tests for the purpose of gaining additional information concerning the product.

If more complete data are desired concerning the methods described here, it is recommended that the original references be consulted.

Antiknock Value Determination.—The five methods given here are those which have been and are being used to some extent for the evaluation of the antiknock properties of aviation gasolines. In addition, supercharged methods have become widely used for this purpose. No information concerning these, however, may be disclosed for the duration of the war.

A.S.T.M.-C.F.R. Motor Method (A.S.T.M. D357-42T).[1]— A tentative test procedure, which has been adopted by the A.S.T.M., is used as an antiknock rating method particularly for motor fuels. However, it has also been used widely in the past few years to rate aviation fuels. Being a tentative standard, the operating conditions and procedure are subject to change before adoption (or rejection) as a standard test method. The testing equipment consists essentially of a single-cylinder constant-speed internal-combustion motor equipped with a variable-compression head, multiple fuel tanks, fuel-air metering device, loading equipment, and various other accessory equipment. (For a complete description of this apparatus, see Ref. 1.)

Octane-number determinations are made in the following manner: The test engine is warmed up and all specified motor conditions are attained before the test is begun. The fuel to be rated is placed in one of the three fuel bowls, and the engine is operated on this fuel while the variable-compression head is adjusted to give a medium knockmeter reading (after the fuel-air ratio is adjusted to give maximum knock for this fuel).

Reference fuel blends of known octane number, and differing from each other no more than two octane numbers, are chosen so that one will give a higher and the other a lower knockmeter reading than is given by the test fuel at that compression ratio. After several readings are taken for each fuel, during which the air-fuel ratios are adjusted to give maximum knock, they are averaged and the octane number of the test fuel is obtained by interpolating the knockmeter readings. The octane number is reported as the nearest whole number, *i.e.*, 82.5 is reported as 82 and 82.6 as 83.

C.F.R. Research Method.[2]—The Cooperative Fuel Research Committee developed a method of rating fuels in regard to antiknock value which differs from the preceding method mainly in conditions of operating the test engine (see Table 2-III). The equipment is essentially the same as that used for the A.S.T.M. Motor method, and the procedure followed to rate an unknown fuel is almost identical. This method of test has been used mainly for rating motor fuels and, in general, is not widely used for aviation-fuel antiknock rating. Much of the basic investigation of knocking tendencies of pure hydrocarbons has been carried out using the C.F.R. method.

A.S.T.M.-C.F.R. Aviation Method (*A.S.T.M.: D614-42T*).[1]— The Aviation method was designed specifically for the purpose of determining octane numbers of aviation fuels. It is at present a tentative A.S.T.M. standard and as such is subject to change before adoption. The test engine used is basically the same type as that used for the Motor method, the difference being in operating conditions and method of determining maximum knock of the test and reference fuels. Instead of a bouncing pin and knockmeter, a thermal plug is used to indicate maximum knock. This makes use of the fact that maximum temperature in the cylinder is approximately coincident with maximum knock and that the relative maximum temperatures caused by various fuels under constant operating conditions are quantitatively indicative of their antiknock values.

The procedure is described as follows: The test fuel is placed in one of the three fuel bowls, and a compression ratio is selected by adjusting the variable-compression head which will give the standard thermal-plug temperature (or slightly below) while the engine is operating on the test fuel at a fuel-air ratio giving

the maximum "knock" (as measured in temperature). Reference fuel blends of known octane number (and known thermal-plug temperature at the compression ratio chosen for the test fuel), differing from one another by no more than two octane numbers, are selected and placed in the other two bowls. The maximum thermal-plug temperatures are determined for each of the three fuels by averaging several readings on each one, and the octane number of the test fuel is determined by interpolation. The octane rating is expressed as an octane number or in terms of isooctane plus milliliters of tetraethyl lead (for octane ratings above 100).

United States Army Method.[4]—The Army method was devised for the use of the armed services of the nation to rate aviation fuels according to their relative antiknock values. The test engine is essentially the same as that used for the A.S.T.M.-C.F.R. Aviation method, the principal difference being that the Army method uses a $2\frac{5}{8}$ by $4\frac{1}{2}$-in. cylinder while the A.S.T.M.-C.F.R. method uses a $3\frac{1}{4}$ by $4\frac{1}{2}$-in. cylinder. The principal differences in test-engine operating conditions are shown in Table 2-III.

The actual test procedure is almost identical with that of the A.S.T.M.-C.F.R. Aviation method. A thermal plug is utilized to determine maximum temperature readings for the test and reference fuels, and the readings are interpolated to determine the octane rating of the test fuel. The antiknock value is reported as octane number or isooctane plus milliliters of tetraethyl lead.

British Air Ministry Method.[5]—The British Air Ministry method was developed for the rating of aviation fuels used by the British Air Force. The equipment used is identical with that used for the A.S.T.M.-C.F.R. Motor method, and the operating conditions vary but slightly (see Table 2-III). The procedure followed in rating an unknown fuel is the same as that for the Motor method.

Color Evaluation.—The Saybolt Color method is used in determining the color of the undyed and "unleaded" fuel. After dyeing and "leading," the color of the fuel is determined by comparison with color standards.

Saybolt Color Method (A.S.T.M.: D156-38).[6]—The Saybolt Color method utilizes the color-matching apparatus described in Ref. 6 and elsewhere. This apparatus consists essentially of

two glass tubes 14 to 16 mm. in diameter. One, 20 in. long, is closed at the bottom with a glass disk in a metal collar provided with a petcock for draining. This tube is graduated in $\frac{1}{8}$-in. graduations and marked in inches. The other, 19 in. in length, is open at both ends and provided with a metal collar at the lower end to hold the standard color glasses. The tubes are mounted in a holder which has a matching eyepiece at the top. Light is reflected up through the tubes by means of a mirror.

The procedure is as follows: The oil tube (graduated tube) is cleansed by rinsing with the sample. It is then filled to a depth of 12 in. with the sample and compared with the standard disk (or disks). After selecting a combination of color glasses (or disks) and a depth of sample slightly darker than the standards, the sample level is lowered by draining from the petcock, until the color of the sample and the standards match. The color is then read from a chart based on the disks used and the depth of the sample. Saybolt colors range numerically from $+30$ to -16, representing water white to light yellow.

Low-temperature Properties.—The low-temperature property determined is that of freezing point.

Freezing Point (Federal Specifications 141.1).[7]—No universal standard method of determination of the freezing point of gasolines has been adopted. Almost any method involving the correct heat-exchange rate between the sample and the cooling medium is satisfactory. A suitable apparatus is described in Ref. 7 and elsewhere. This consists essentially of a Dewar flask into which is fitted a stopper containing a smaller double-walled glass tube fitted with a glass tube connected to the annular space between the walls. By applying vacuum to this tube, the air pressure in the annular space may be varied, thereby controlling the heat-transfer rate through it. The small tube is equipped with a stopper containing a thermometer and a stirring device. The stirring device is a wire which is passed through a packing gland (a brass tube inserted in the stopper) packed with cotton. This is necessary to prevent condensed moisture from entering the sample.

The procedure is as follows: 15 ml. of sample is poured into the small tube and the tube inserted in the Dewar flask containing the cooling medium (solid CO_2 and acetone). The sample is stirred continuously until crystalline materials appear, and the

temperature at which these first appear is designated as the freezing point.

Because of the low temperatures involved, care should be taken that no outside moisture is allowed to contaminate the sample. Sometimes a slight cloud will form above the actual freezing point owing to traces of contained moisture. This is not the true freezing point.

Stability—Gum Formation.—Classed under this heading are found methods of test used to determine the gum stability or oxidation resistance of the fuel. Although the oxygen-bomb test and copper-dish test are the ones usually specified, the others given are widely used as accessory methods.

A.S.T.M. Air Evaporation Method (A.S.T.M.: D381-42).[8]— This method is adapted to the determination of the amount of gum present in the gasoline at the time of test. The equipment consists of an insulated bath, closed except for a vapor outlet equipped with a reflux condenser and a well capable of containing a special tall-form 100-ml. beaker. The bath is filled with some liquid boiling between 320 to 330°F. (Ethylene glycol is suitable.) Inside the bath, immersed in the liquid and around the beaker well, is the air-supply line in the form of a coil. This line extends out of the top of the bath and down over the surface of the sample in the beaker. Heat is supplied to the bottom of the bath by means of a suitable electric heater. The air flow is measured by a suitable calibrated flow meter in the air line.

The procedure is as follows: The weighed beaker is placed in the well of the hot bath and the air rate adjusted to 1 liter per sec. ±15 per cent. Fifty milliliters of gasoline is poured into the beaker and evaporated. The beaker is then removed, after remaining in the bath 15 min. after the gasoline has evaporated, and weighed. The weight of the residue is reported in milligrams per 100 ml.

Copper-dish Gum Test (F.S.: 530.11).[9]—The copper-dish test test was developed for the determination of the presence of corrosive materials in the fuel and also gum content. This is identical with the Federal Specification for Lubricants and Liquid Fuels 530.11. The apparatus required is a hemispherical copper dish approximately $3\frac{1}{2}$ in. in diameter and a steam bath capable of covering the lower side of the dish up to the level of the gasoline sample.

The procedure is as follows: The highly polished, clean copper dish is weighed and 100 ml. of the gasoline is poured into it. The dish and contents are placed on the steam bath and the gasoline evaporated. The dish is then removed and weighed. The residue is reported in milligrams per 100 ml. and notation made as to the color of the inside of the dish. Black or gray discoloration usually indicates the presence of sulfur.

A.S.T.M. Induction Period Test (*D*525-41*T*).[10]—The A.S.T.M. tentative gum-stability method is used to determine the tendency of a gasoline to form gum in storage. The apparatus necessary is a steel bomb capable of withstanding a pressure of 180 lb. at 212°F. equipped with a glass liner and a lid equipped with a filling rod with connections for a recording or indicating gauge and a valve through which oxygen is admitted. A boiling water bath is used for immersion of the bomb during the test.

In making the test, the bomb is thoroughly cleaned and dried and 50 ml. $\pm$ 1 ml. of sample is poured into it (into the glass liner). The top is put on and made secure and the gauge and oxygen supply connections made. Oxygen is admitted to the bomb at a pressure of 125 lb. per sq. in. and after 10 min. the pressure is adjusted to 100 $\pm$ 2 lb. per sq. in. The bomb is then immersed in the boiling water bath and the time of immersion taken as the starting time. If an indicating pressure gauge is used, pressure readings are taken at 15-min. intervals. The break point is taken as the point preceded by a pressure drop of exactly 2 lb. per sq. in. and succeeded by a drop of not less than 2 lb. per sq. in. The number of minutes from the start of the test to the break point is recorded and the observed temperatures averaged. The induction period is calculated on the basis of 212°F. and reported in minutes.

Accelerated Gum Test.[11]—The accelerated aging test for gasoline is another of the methods proposed for the indication of the gum-forming tendency of gasoline in storage.

The apparatus used consists of a bomb of sufficient capacity to hold an 8-oz. sample bottle and capable of withstanding pressures of around 180 lb. per sq. in. It is equipped with a pressure gauge, oxygen inlet line, and a valve. A boiling water bath or steam bath of sufficient capacity for complete immersion of the bomb is used.

To conduct the test the following procedure is carried out: A clean steel strip or tubing furnishing 35 sq. in. of surface is twisted to prevent flat contact and placed in the 8-oz. sample bottle. Two hundred milliliters of gasoline is poured into the sample bottle and the bottle covered loosely and placed in the bomb. The bomb is then closed and filled with oxygen to a pressure of 95 to 100 lb. per sq. in. after the air is purged by displacement with oxygen. The bomb is then immersed in the steam or boiling water bath and maintained at a temperature of 208 to 212°F. for a period of 5 hr. The bomb is removed and cooled at the end of this period and the pressure is released. The contents of the bottle are poured out and the insoluble gum is dissolved with acetone and benzene mixture. The washings are added to the gasoline, and one-half of the total is evaporated in a weighed glass dish on a steam bath. After evaporation, the dish and its contents are dried in an oven and weighed. The gum is reported in milligrams per 100 ml. If tetraethyl lead is present and the amount of gum is over 6 mg. per 100 ml., the amount of lead in the residue must be determined and its weight deducted from the weight of the residue.

A.S.T.M. Acid Heat Test (A.S.T.M. D481-39).[12]—The acid heat test was developed for the purpose of indicating approximately the amount of unsaturated hydrocarbons in gasoline which are capable of reacting with sulfuric acid under the conditions of test.

The apparatus consists of a thermos bottle having a capacity of 450 to 470 ml. and equipped with a special screw cap having an opening in the top to permit holding a rubber stopper through which is inserted a thermometer and a glass stopcock for pressure releaes. The cap is provided with a washer to hold the rubber stopper firmly in the neck of the bottle when the cap is screwed down.

The test is conducted as follows: 150 ml. of the sample is measured into the thermos in case the acid heat is 50°F. or less. [With samples having acid heats of 50 to 100°F., 75 ml. of sample and 75 ml. of kerosene (acid heat less than 5°F.) and with samples having acid heats above 100°F., 50 ml. of sample and 100 ml. of kerosene are used.] Thirty milliliters of 93 per cent H_2SO_4 at exactly the same temperature as the gasoline is poured into the bottle and the stopper inserted and the screw cap

tightened. The mixture is shaken at a prescribed rate and in a prescribed manner for 3 min. and the temperature is recorded at the end of 10 min. after the end of the shaking period. The difference between the initial temperature and the highest temperature is reported as acid heat, in degrees Fahrenheit. In the diluted samples the difference is multiplied by 2 or 3, as the case may be, and reported as acid heat 1:1 or 1:2, °F.

Modified Acid Heat Test (Nitration).[13]—A modified acid heat test which uses a nitrating mixture instead of the regular sulfuric acid has been used by some commercial laboratories in place of the regular acid heat test.

The apparatus and procedure for the test are the same as for the conventional acid heat test. Instead of 30 ml. of 93 per cent H_2SO_4 added to 150 ml. of sample (or sample and blank blend), however, 20 ml. of nitrating acid, composed of 75 per cent concentrated sulfuric acid and 25 per cent concentrated nitric acid is added to 50 cc. of the sample. The difference between the initial and maximum temperatures is reported as the acid heat in degrees Fahrenheit.

Sulfur Content and Corrosiveness.—The total sulfur content of an aviation fuel is determined by the Lamp Sulfur method. Corrosiveness is usually determined by the Copper-strip Corrosion method and also by the Copper-dish Gum method, described on pages 37, and 35, respectively.

Sulfur Content (A.S.T.M. D90-41T).[14]—The sulfur content of aviation fuel is determined by the Lamp Sulfur method, which is an A.S.T.M. tentative standard.

The apparatus consists of a 25-ml. Erlenmeyer flask as a sample container, a special glass burner, a chimney, an absorber, and a spray trap equipped with a tube for connection with a manifold, all fitted together with suitable ground-glass joints. The burner is a wick burner with the wick extending into the sample container (described in detail in Ref. 14).

The test procedure is as follows: Approximately 10 grams of sample is added to the sample flask, the burner is assembled to the flask and the whole assembly weighed. Forty milliliters of neutralized hydrogen peroxide is added to the absorber. The apparatus is assembled and the lamp is lighted and the air pressure on the burner and the vacuum on the spray trap are adjusted according to specifications. The sample is burned

until it is almost depleted and then the flask and burner assembly is disconnected and weighed. The contents of the absorber are titrated with a standard sodium hydroxide solution and the amount of sulfur calculated and reported in per cent. (The sulfur dioxide formed on burning of the sulfur in the sample is oxidized to sulfur trioxide and hydrated to sulfuric acid.)

Copper-strip Corrosion (A.S.T.M. D130-30).[15]—This method was devised for the purpose of determining elemental and corrosive sulfur compounds in motor fuel. The procedure consists of placing a clean polished copper strip approximately 3 in. long and ½ in. wide in a suitable bottle or test tube and filling the bottle with gasoline so that the strip is completely covered. The bottle is then immersed for 3 hr. in a bath held at 122°F. The strip is then removed and compared with a fresh strip. Any evidence of corrosion is reported.

This test in conjunction with the copper-dish test and total sulfur determination indicates the fuel's tendency toward corrosiveness.

Vaporization Characteristics.—The vaporization characteristics of an aviation fuel are determined by the A.S.T.M. Distillation method and the vapor pressure by the Reid Vapor Pressure method.

Distillation (A.S.T.M. D86-40).[16]—The apparatus used in this method of test consists of a special 100-ml. side-arm distillation flask, a condenser box containing a straight condenser tube, a special burner and flask shield, a burner or electric heater, and a graduated cylinder for a receiver (described in Ref. 16).

In making the test, 100 ml. of the sample at 60°F. is poured into the distillation flask and the cork containing the thermometer is inserted into the neck of the flask. The heat source is adjusted so that the first drop of distillate appears between 5 and 10 min. after the start of heating. The condenser is maintained at 32 to 40°F. The temperature at which the first drop appears is taken as the *initial boiling point*. The heat source is then adjusted so that distillation proceeds at a rate of 4 to 5 ml. per min. The volume in the receiver is recorded at each 10°C. or 10°F. equivalent or the temperature is read at each 10 per cent increase in volume of distillate or both. The maximum temperature reached by the thermometer is called the *end point*. The volume in the receiver is read and reported as *recovery*.

The volume of the residue cooled and poured from the distillation flask is measured and reported as *residue*. The loss is reported as the difference between the sum of the per cent recovery plus per cent residue. Since the loss is due to the lighter materials, the loss may be added to the percentage recovered at any temperature and be designated as *per cent evaporated*. If the loss is not included, the volumes are reported as *per cent recovered*.

Vapor Pressure (A.S.T.M. D323-42).[17]—The apparatus for determining vapor pressure consists of a vapor-pressure bomb assembly made up of a sample chamber, an air chamber, and a gauge. A cooling bath for the gasoline chamber and sample container is provided and its temperature is maintained at 32 to 40°F. The water bath in which the bomb is immersed during the test is maintained at 100°F.

The test is conducted as follows: The gauge is screwed tightly to the air chamber and the temperature of the air chamber is determined by means of a thermometer. The cooled sample chamber is filled to overflowing with the chilled sample and the air chamber and gauge assembly screwed tightly to the sample chamber. The whole assembly is shaken vigorously and then immersed in the water bath (100°F.). At the end of 5 min. the assembly is shaken again and replaced in the bath. This is repeated until the gauge readings become constant. The pressure read from the gauge is corrected according to barometric reading and initial air temperature and reported as Reid vapor pressure.

Extreme care should be taken in sampling, pouring, and conducting the test since small changes in composition change the vapor pressure.

Miscellaneous Test Methods.—Other tests generally used for the evaluation of various properties of aviation fuels are those used to determine the calorific value, specific gravity, tetraethyl lead content, and water miscibility.

Combustion Value (A.S.T.M. D240-39,[18] Modified[19]).—The combustion value of aviation fuels is determined by the bomb-calorimeter method. The apparatus required consists of a calorimeter vessel equipped with a suitable mechanical stirring device, a calorimeter bomb having a capacity of 300 ml., and an oil sample cup. The regular procedure is modified somewhat for the determination of combustion value of volatile fuels in that a

gelatine capsule is filled with cotton and the cotton saturated with the fuel. The capsule and cotton are weighed first empty and then containing the fuel in order to get the weight of the sample. The ignition wire is wrapped around the capsule and placed in the bomb and connected. The bomb is filled with oxygen at 30 atm. The sample is fired electrically and the temperature rise in the water around the bomb determined. From this and other correction data the calorific value of the fuel is calculated and reported as B.t.u.'s per pound or B.t.u.'s per gallon. This is the gross calorific value for the fuel. To calculate the net value, the weight of water formed per pound of fuel burned must be determined by some suitable method. The net value would then be the gross calorific value in B.t.u. per pound minus the weight of water (in pounds) formed in burning 1 lb. of fuel times 1050.

A.P.I. Gravity—Specific Gravity (A.S.T.M. D287-39).[20]—The specific gravity of aviation fuel is determined by calculation or conversion from A.P.I. gravity. The A.P.I. gravity is determined by means of special standard hydrometers and corrected to a temperature of 60°F. The relationship between A.P.I. and specific gravity is shown by the following formula:

$$\text{A.P.I.} = \frac{141.5}{\text{sp. gr. } 60\!/\!60°\text{F.}} - 131.5$$

Tables are available showing the equivalent of A.P.I. in specific gravity and pounds per gallon throughout the range.

The procedure consists of pouring the sample into a suitable glass cylinder, inserting the hydrometer having the proper range, reading the hydrometer graduation level with the top of the sample, and reading the temperature of the sample. The readings are corrected to 60°F. by means of a standard table.

Tetraethyl Lead Content (A.S.T.M. D526-42).[21]—This method was designed for the determination of tetraethyl lead in gasoline and volatile fuels.

The equipment consists of a special 500-ml. boiling flask equipped with a Hopkins reflux condenser, a thistle tube with stopcock, and a heating tube welded on to the bottom of the boiling flask with a stopcock for draining (described in detail in Ref. 21).

The procedure is as follows: 50 ml. of gasoline and 50 cc. of heavy distillate (10 per cent evaporated at 400°F., 90 per cent at 460°F.) are added to the flask through the thistle tube. Fifty milliliters of HCl (sp. gr., 1.19) is added and the mixture is refluxed for 30 min. The acid is drained off and the gasoline is twice refluxed with distilled water (50-cc. portions). The washings are added to the acid in a beaker and the total mixture is evaporated to dryness. The residue is treated with nitric acid until a white salt of $PbCl_2$ is obtained. The salt is then dissolved in 10 ml. of concentrated nitric acid and the lead content is determined by titration or by gravimetric methods as the chromate or sulfate.

Water Tolerance.[22]—Water tolerance or miscibility of an aviation fuel is determined by shaking 20 ml. of distilled water and 80 ml. of fuel in a glass-stoppered graduate for 2 min. After settling, the change in volume of either phase is read.

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